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ENVIRO
Technical
Information for
Problem
Spills

VINYL CHLORIDE

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ENVIRONMENTAL AND TECHNICAL INFORMATION FOR PROBLEM SPILLS MANUALS

The Environmental and Technical Information for Problem Spills (EnviroTIPS) manuals provide detailed information on chemical substances. This information is intended to assist the reader in designing countermeasures for spills and to assess their impact on the environment. The report has been reviewed by the Technical Services Branch, Environmental Protection Service, and approved for publication. Approval does not signify that the contents reflect the views and policies of the Environmental Protection Service. Mention of trade names or commercial products does not constitute endorsement for use.

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VINYL CHLORIDE

ENVIRONMENTAL AND TECHNICAL INFORMATION FOR PROBLEM SPILLS

Technical Services Branch
Environmental Protection Programs Directorate
Environmental Protection Service
Ottawa, Ontario

March 1985

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FOREWORD

The Environmental and Technical Information for Problem Spills (EnviroTIPS) manuals were initiated in 1981 to provide comprehensive information on chemicals that are spilled frequently in Canada. The manuals are intended to be used by spill specialists for designing countermeasures for spills and to assess their effects on the environment. The major focus of EnviroTIPS manuals is environmental. The manuals are not intended to be used by first-response personnel because of the length and technical content; a number of manuals intended for first-response use are available. The information presented in this manual was largely obtained from literature review. Efforts were made, both in compilation and in review, to ensure that the information is as correct as possible. Publication of these data does not signify that they are recommended by the Government of Canada, nor by any other group.

ACKNOWLEDGEMENTS

The final version of this manual was prepared by the staff of the Environmental Protection Service who wrote extensive revisions to the text, drafted illustrations and incorporated all comments and additions.

The level of detail present was made possible by the many individuals, organizations and associations who provided technical data and comments throughout the compilation and subsequent review of and input to this manual. The draft of this manual was prepared under contract to Environment Canada by M.M. Dillon Consulting Engineers and Planners, Concord Scientific Corporation and Waterloo Engineering Limited.

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1 SUMMARY

VINYL CHLORIDE ($H_2C=CHCl$)

Colourless gas with a mild, sweet odour

SYNONYMS

VCM, VC, Chlorethene, Chloroethene, Chloroethylene, Vinyl Chloride Monomer, Vinyl C Monomer, Monochloro Ethylene, Monochloroethene, Ethylene Monochloride, Chlorure de Vinyle (Fr.)

IDENTIFICATION NUMBERS

UN No. 1086; CAS No. 75-01-4; OHM-TADS No. 7216947; STCC No. 4905792

GRADES & PURITIES

Commercial or Technical grade, purity 99.9 percent

IMMEDIATE CONCERNS

Fire: Highly flammable. Flashback along vapour trail may occur

Human Health: Human carcinogen; toxic by inhalation and skin contact

Environmental: Harmful to aquatic life

PHYSICAL PROPERTY DATA

Shipping State: liquid (compressed gas)
State (15°C, 1 atm): gas
Boiling Point: -13.4°C
Melting Point: -153.8°C
Flammability: flammable
Flash Point: -78°C (OC)
Vapour Pressure: 336.5 kPa (20°C)
Density: 0.969 g/cm^3 (liquid at -14°C)
2.62 kg/m^3 (gas at 25°C)
Solubility (in water): 0.11 g/100 g H_2O (25°C)

Behaviour (in water): floats and boils; no reaction
Behaviour (in air): vapour is heavier than air
Odour Threshold Range: 1200 to 25 000 ppm
Polymerization: occurs if heated, in sunlight or presence of air; reaction is exothermic

ENVIRONMENTAL CONCERNS

In aquatic systems, vinyl chloride evaporates rapidly and degrades very slowly. Fish may bioconcentrate it by a factor of up to 1.9.

HUMAN HEALTH

TLV®: 5 ppm (10 mg/m^3)
IDLH: not established

Exposure Effects

Inhalation: Irritation to eyes, nose and throat. Causes dizziness, anesthesia, difficult breathing, lung irritation, headache and paralysis. Large concentrations may be fatal.

Contact: Irritation to skin and eyes. Contact with liquid causes frostbite and dry skin. Contact with eyes will cause inflammation of conjunctiva.

IMMEDIATE ACTION

Spill Control

Restrict access to spill site. Issue warning: "FLAMMABLE". Call fire department and notify manufacturer. Eliminate sources of ignition including traffic and equipment. Stop the flow and contain spill, if safe to do so. Avoid contact with liquid and inhalation of vapour; stay upwind of release. Keep contaminated water from entering sewers or watercourses.

Fire Control

Do not extinguish fire unless release can be stopped. Use foam, dry chemical, carbon dioxide, water spray or fog to extinguish. Cool fire-exposed containers with water. Containers may explode in heat of fire. Stay clear of tank ends.

COUNTERMEASURES

Emergency Control Procedures in/on

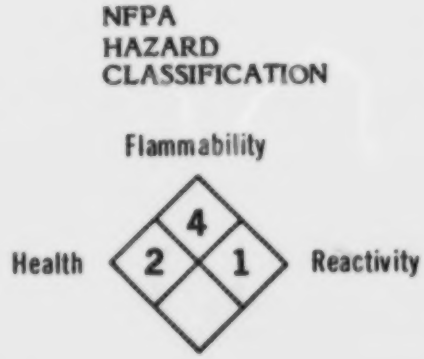
Soil: Construct barriers to contain spill. Remove contained liquid - if possible and using extreme caution - with pumps to vinyl chloride tanks. Otherwise, let evaporate.

Water: Contain contaminated water with dams or natural barriers. After VCM levels in water are low, release water.

Air: Use water spray to control flammable vapour. Control runoff to ensure it does not enter sewers or water courses until almost all VCM is evaporated.

NAS HAZARD RATING

Category	Rating
Fire	4
Health	
Vapour Irritant	2
Liquid or Solid Irritant	1
Poison	2
Water Pollution	
Human Toxicity	0
Aquatic Toxicity	0
Aesthetic Effect	0
Reactivity	
Other Chemicals	2
Water	0
Self-reaction	2



2 PHYSICAL AND CHEMICAL DATA

Physical State Properties

Appearance	Colourless gas or liquid under pressure (Dow MSDS 1980)
Usual shipping state	Liquid: liquefied compressed gas (HCG 1981)
Physical state at 15°C, 1 atm	Gas
Melting point	-153.8°C (HCG 1981; Kirk-Othmer 1983)
Boiling point	-13.4°C (HCG 1981; Kirk-Othmer 1983)
Vapour pressure	336.5 kPa (20°C) (Dow MSDS 1980) 115 kPa (-10°C) (Kirk-Othmer 1983)

Densities

Density	0.969 g/cm^3 (liquid at -14.2°C) (Kirk-Othmer 1983) 0.908.4 g/cm^3 (liquid at 21°C) (HCG 1981) 2.62 kg/m^3 (gas at 25°C) (Matheson 1980)
Specific gravity	0.9104 (liquid 20°/20°C) (Dow MSDS 1980)
Vapour density	2.15 (Dow MSDS 1980) 2.21 (25°C) (Matheson 1980)

Fire Properties

Flammability	Highly flammable (NFPA 1978) -78°C (Cleveland open cup) (DPIMR 1981)
Autoignition temperature	472°C (NFPA 1978)
Burning rate	4.3 mm/min (CHRIS 1978)
Upper flammability limit	33.0 percent (v/v) (NFPA 1978) 22 percent (v/v) (Kirk-Othmer 1983; Matheson 1980)
Lower flammability limit	3.6 percent (v/v) (NFPA 1978)
Heat of combustion	1134 kJ/mole (20°C) (CRC 1980)
Combustion products	Carbon dioxide, water and hydrogen chloride (CRC 1980)
Flashback potential	May travel considerable distance to a source of ignition and flash back (NFPA 1978)

Explosiveness	Forms explosive mixtures with air (NFPA 1978)
Behaviour in a fire	At elevated temperatures, polymerization may take place with possible container rupture (NFPA 1978)
Electrical ignition hazard	May be ignited by static discharge (NFPA 1978)

Other Properties

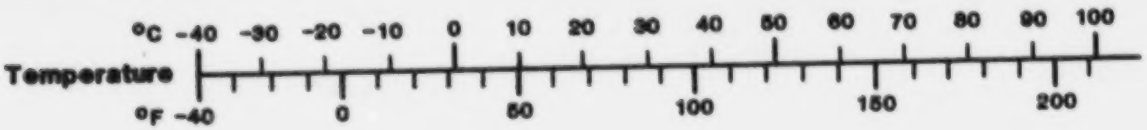
Molecular weight of pure substance	62.499 (Kirk-Othmer 1983)
Constituent components of typical commercial grade	99.9 percent vinyl chloride (Dow MSDS 1980)
Refractive index	1.366 (liquid at 20°C) (Ullmann 1975)
Viscosity	Liquid: 0.273 mPa•s (-20°C) (Kirk-Othmer 1983) Gas: 0.0107 mPa•s (20°C) (Matheson 1980)
Liquid interfacial tension with air	16.0 mN/m (25°C) (CHRIS 1978) 23.1 mN/m (-20°C) (Matheson 1980)
Liquid interfacial tension with water (est.)	30 mN/m (20°C) (CHRIS 1978)
Latent heat of fusion	4.74 kJ/mole (at melting point) (HCG 1981)
Latent heat of sublimation	25.65 kJ/mole (est.)
Latent heat of vaporization	20.62 kJ/mole (at boiling point) (Kirk-Othmer 1983)
Heat of polymerization	4.45 kJ/mole (-150°C), 71.18 kJ/mole (156.6°C) (Ullmann 1975)
Polymerization expansion	About 35 percent (Ullmann 1975)
Heat of formation	37.3 kJ/mole (25°C) (Sussex 1977)
Ionization potential	10.0 eV (Rosenstock 1977)
Heat capacity constant pressure (C_p)	53.6 J/(mole•°C) (25°C) (HCG 1981) 84.5 J/(mole•°C) (liquid at 20°C) (Kirk-Othmer 1983)
constant volume (C_v)	50.6 J/(mole•°C) (25°C) (HCG 1981)
Critical pressure	5600 kPa (Kirk-Othmer 1983)
Critical temperature	156.6°C (Kirk-Othmer 1983)
Thermal conductivity	7.95×10^{-3} W/(m•K) (25°C, gas) (Matheson 1980)
Saturation concentration	8625 g/m^3 (20°C) (calc.)

Dipole moment	1.499 D (Kirk-Othmer 1983)
Dielectric constant	6.26 (17.2°C) (Ullmann 1975)
Solubility	
In water	0.11 g/100 g H_2O (25°C) (Kirk-Othmer 1983)
In other common materials	Very soluble in diethyl ether, soluble in ethanol (CRC 1980) Soluble in methanol (Ullmann 1983)
Of water in vinyl chloride	0.03 g/100 g vinyl chloride (-15°C) (Kirk-Othmer 1983)
Vapour Weight to Volume Conversion Factor	1 ppm = 2.577 mg/m^3 (20°C) (Verschueren 1984)

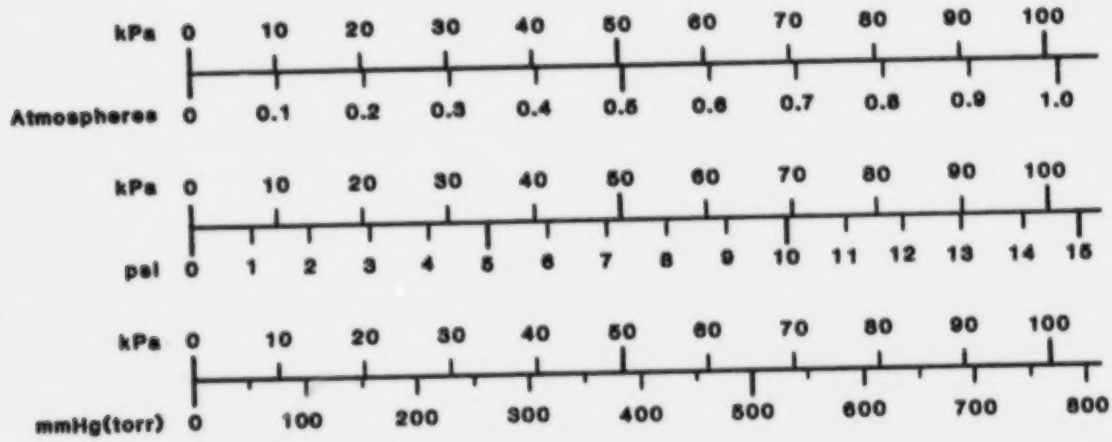
TABLE 1

VINYL CHLORIDE

CONVERSION NOMOGRAMS



Pressure 1 kPa = 1 000 Pa



Viscosity

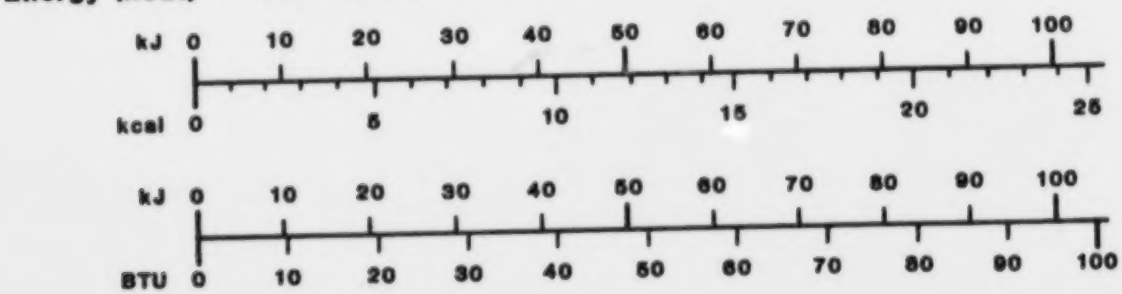
Dynamic 1 Pa·s = 1 000 centipoise (cP)

Kinematic 1 m^2/s = 1 000 000 centistokes (cSt)

Concentration (in water)

1 ppm ≅ 1 mg/L

Energy (heat) 1 kJ = 1 000 J



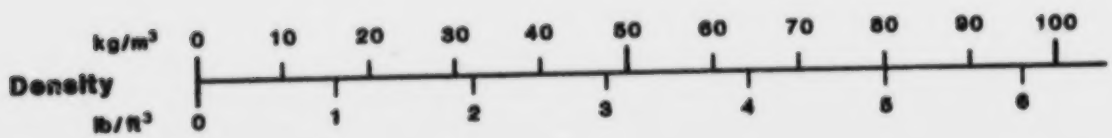


FIGURE 1

VINYL CHLORIDE

VAPOUR PRESSURE

Reference: PPH 1974

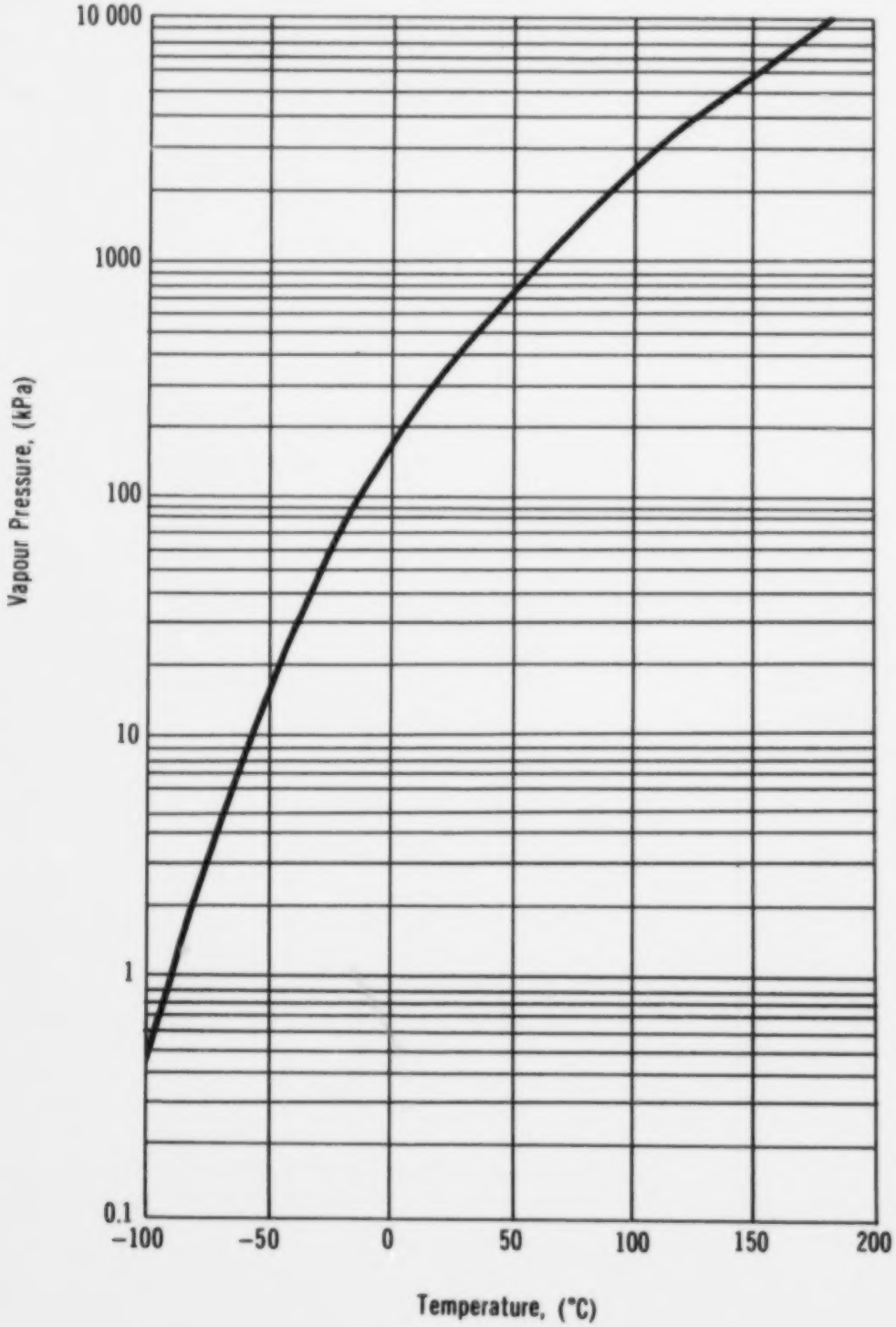


FIGURE 2

VINYL CHLORIDE

SOLUBILITY IN WATER

Reference: MATHESON 1974; KIRK-OTHMER 1983

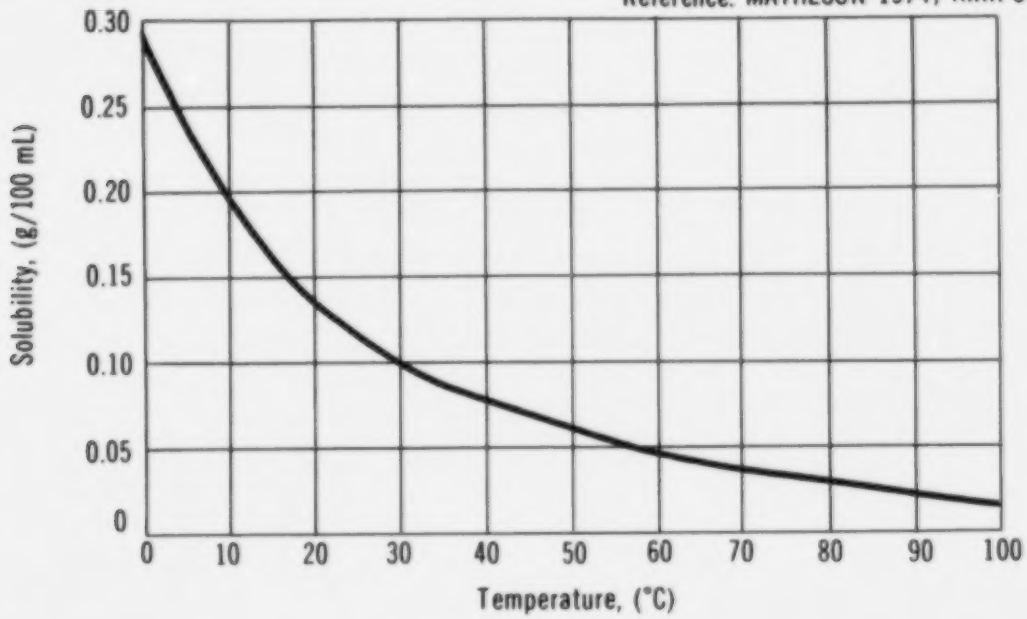


FIGURE 3

VINYL CHLORIDE

LIQUID DENSITY

Reference: PPH 1974; ULLMANN 1975

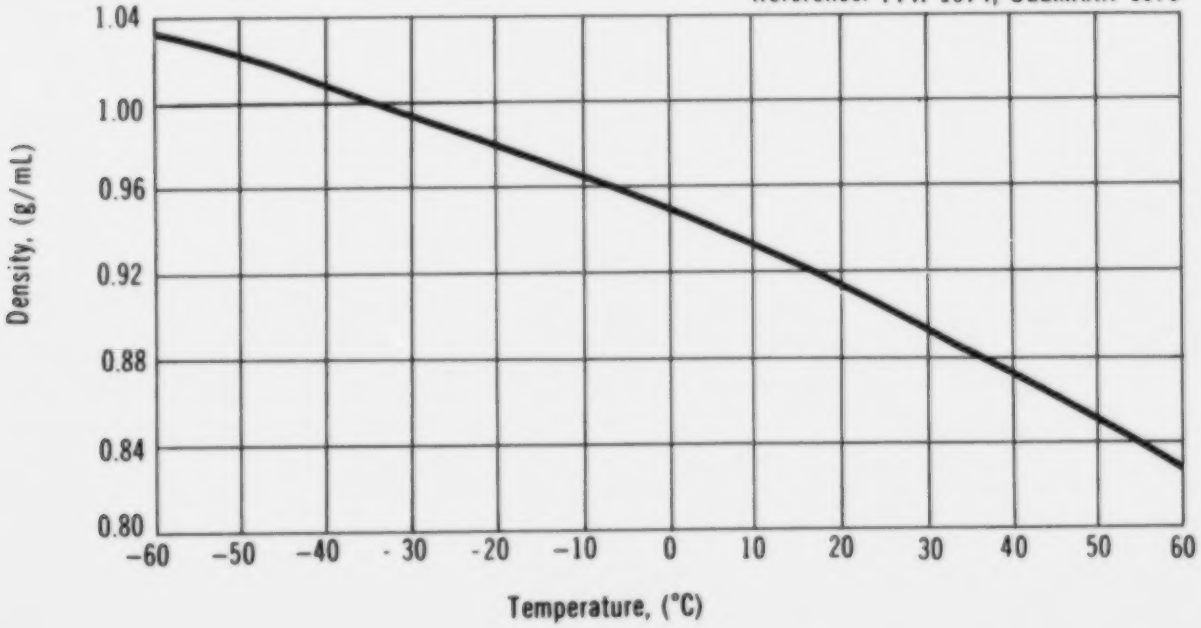


FIGURE 4

VINYL CHLORIDE

LIQUID VISCOSITY

Reference: ULLMANN 1975; KIRK-OTHMER 1983

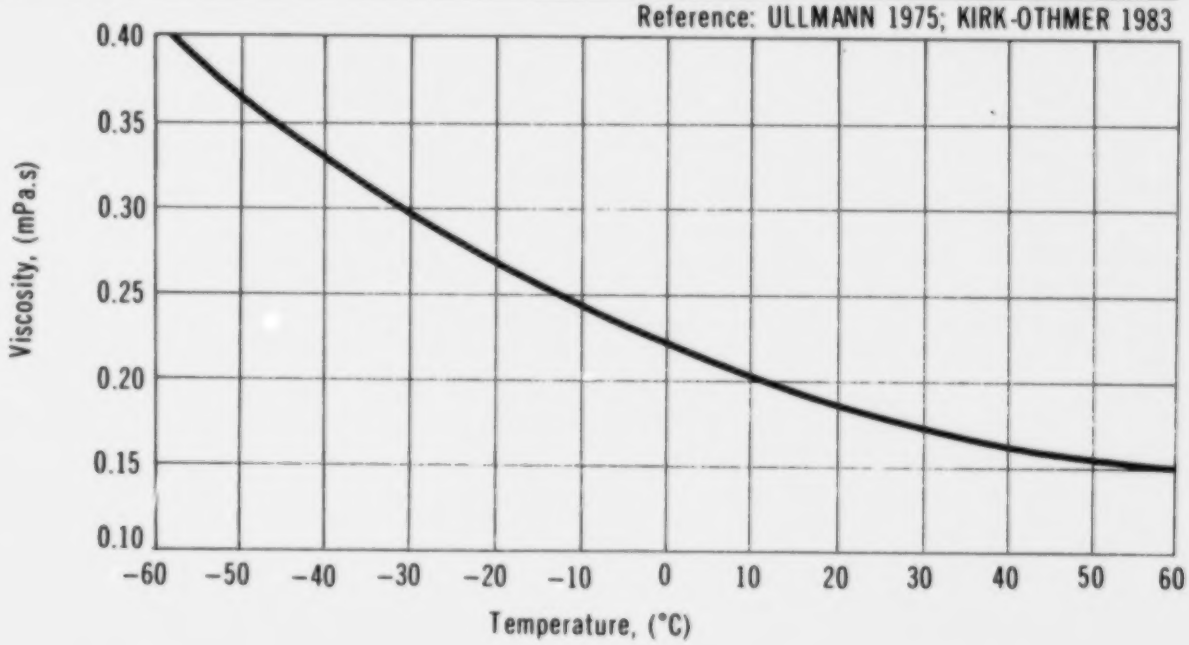
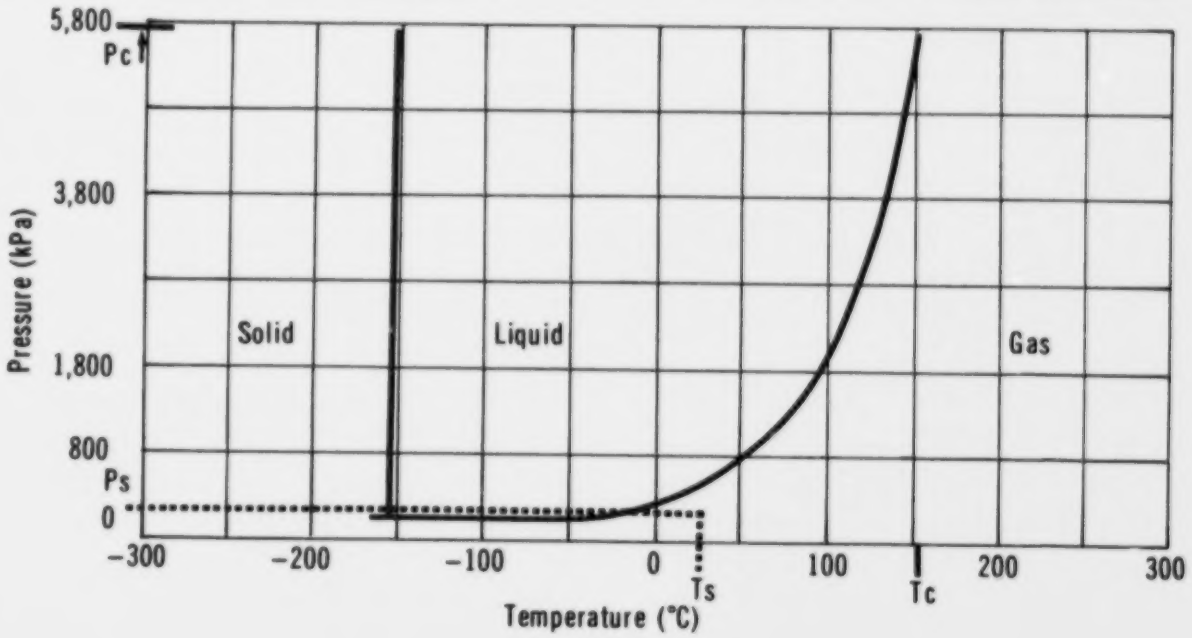


FIGURE 5

VINYL CHLORIDE

PHASE DIAGRAM



3 COMMERCE AND PRODUCTION

3.1 Grades, Purities (Dow MSDS 1980; MCA 1972; Kirk-Othmer 1983)

Vinyl chloride monomer is commonly sold as a liquefied gas, in a commercial or technical grade with a purity of 99.9 percent. The following are the maximum levels of impurities found in vinyl chloride:

Impurity	Maximum level, ppm
Acetylene	2.0
Acidity, as HCl by wt.	0.5
Acetaldehyde	0.0
Alkalinity, as NaOH by wt.	0.3
Butadiene	6.0
1-Butene	3.0
2-Butene	0.5
Ethylene	4.0
Ethylene dichloride (EDC)	10.0
Nonvolatiles	150.0
Propylene	8.0
Water	200.0
Iron, by wt.	0.25

3.2 Domestic Manufacturer (Corpus 1983; Scott 1979)

Dow Chemical Canada Inc.
Box 1012, Modeland Road,
Sarnia, Ontario
N7T 7K7
(519) 339-3131

3.3 Other Suppliers (CGB 1980)

Henley Chemicals Ltd.
1735 Bayly Street
Pickering, Ontario
L1W 3G7
(416) 831-3341

Kingsley and Keith (Canada) Ltd.
310 Victoria Avenue
Montreal, Quebec
H3Z 2M8
(514) 487-1550

St. Lawrence Chemical Co. (Sales) Ltd.
5405 Pare Street
Montreal, Quebec
H4P 1P7
(514) 731-3628

3.4 Major Transportation Routes

Current Canadian production of vinyl chloride is located in Sarnia, Ontario, and Fort Saskatchewan, Alberta. The market area is in Ontario, Quebec and Alberta. The product is most commonly shipped in railway tank cars.

3.5 Production Levels (Corpus 1983)

Company, Plant Location	Nameplate Capacity kilotonnes/yr (1982)
Dow Chemical Canada, Sarnia, Ont.	100
Dow Chemical Canada, Fort Saskatchewan, Alta.	320
TOTAL	420
Domestic Production (1982)	231
Imports (1982)	-
TOTAL SUPPLY	231

3.6 Manufacture of Vinyl Chloride (Kirk-Othmer 1983; FKC 1975; EPA 1978)

3.6.1 General. Vinyl chloride is most commonly made by the "balanced process" in which ethylene is reacted to produce ethylene dichloride which in turn is dehydrochlorinated to produce vinyl chloride.

3.6.2 Raw Materials. The raw materials used in the manufacture of vinyl chloride are ethylene and hydrogen chloride.

3.6.3 Manufacturing Process. Ethylene is reacted with hydrogen chloride and oxygen (sometimes from air; however, pure oxygen is now preferred because of the lower emissions) to produce ethylene dichloride. The reaction is usually carried out in the vapour phase over catalysts containing copper chloride as the active catalyst. The overall reaction is as follows:

$$CH_2{=}CH_2 + 2HCl + 1/2\ O_2 \rightarrow ClCH_2CH_2Cl + H_2O$$

The ethylene dichloride is purified to remove any $FeCl_3$ (which poisons catalysts in the next phase) and is reacted at 2500-3000 kPa at temperatures of 425-550°C to yield vinyl chloride and hydrogen chloride. The hydrogen chloride is recycled to the first step (thus the name "balanced process" for this entire procedure).

The pyrolysis step results in a conversion of 50-60 percent per pass, with a residence time of 2-30 seconds. The following is the pyrolysis reaction:

$$ClCH_2CH_2Cl \rightarrow CH_2{=}CHCl + HCl$$

The resulting vinyl chloride is purified by distillation to remove the by-products (unreacted material, chlorinated hydrocarbons, hydrocarbons).

3.7 Major Uses in Canada (Corpus 1983)

Vinyl chloride is used in the production of polyvinyl chloride and 1,1,1-trichloroethane. In 1982, 86 percent of domestic production was used for polyvinyl chloride manufacture, 4 percent was used for 1,1,1-trichloroethane manufacture, and 10 percent was exported.

3.8 Major Buyers in Canada (Corpus 1983)

Esso Chemical Canada, Sarnia, Ont.
BF Goodrich Canada, Niagara Falls, Ont.; Shawinigan, Que.
Novacor/DSAG, Ft. Saskatchewan, Alta.

4 MATERIAL HANDLING AND COMPATIBILITY

4.1 Containers and Transportation Vessels

4.1.1 General. Liquid vinyl chloride is transported in steel containers and vessels equipped with safety devices and pressure tested at regular intervals. The sole Canadian manufacturer distributes vinyl chloride only by railway tank car; however, as cylinders or tank motor vehicles are occasionally used by distributors, these will also be covered (CCPA 1983).

4.1.2 Cylinders. Vinyl chloride cylinders are of steel construction with net mass usually from 0.45 to 68.2 kg (1 to 150 lb.). A 68.2 kg (150 lb.) cylinder has a tare weight of 63.6 kg (140 lb.), a diameter of 260 mm (10 in.) and a length of 1400 mm (55 in.). Cylinders must comply with specifications as described in Table 2 (RTDCR 1974; HMR 1978). Class 3A and 3AA cylinders having higher service pressures also may be used. Laboratory cylinders are equipped with a CGA valve out connection No. 290 having a thread size of 1.9 cm (0.745 in.) with left hand thread accepting a bullet-shaped nipple. Lecture bottles have a special 0.8 cm (5/16 in.), 32 thread per inch, female outlet (Matheson 1980).

4.1.3 Ton Container. The ton container is a welded steel tank (or cylinder) carrying a net mass of 909 kg (2000 lb.). It must comply with specification 106A500X which states that the container must have a fusion-welded longitudinal seam and a forge welded head seam, pressure tested at 3450 kPa (500 psi) (TCM 1979). Dimensions of the ton container are 207 cm (81-1/2 in.) long by 74.3 cm (29-1/4 in.) diameter. The heads are convex inward. The sides are crimped inward to each end to form chimes which provide a substantial grip for lifting beams. The container is equipped with two identical valves near the centre of one end. The ton container valve differs from the cylinder valve only in that it has no fusible metal plug and has a larger internal passage. Each valve connects with an internal eduction pipe. The valves are protected by a removable steel valve protection hood. All containers are equipped with fusible metal type safety relief devices. Most have six fusible metal plugs, three in each end, spaced 120° apart. The fusible metal is designed to melt between 70 and 73.9°C.

4.1.4 Railway Tank Cars. Railway tank cars must comply with specifications as described in Table 3 (RTDCR 1974). A typical 105A300W railway tank car is illustrated in Figure 6; Table 4 indicates railway tank car details associated with this drawing.

TABLE 2 CYLINDER SPECIFICATIONS

CTC/DOT* Specification lumber	Description
3A150	Seamless steel cylinder. Maximum service pressure 1035 kPa (150 psi).
3AA150	Seamless steel cylinder. Maximum service pressure 1035 kPa (150 psi). Steels definitely prescribed. Maximum carbon content 0.28%.
3E1800	Seamless steel cylinder. Maximum service pressure 12 400 kPa (1800 psi) Maximum diameter: 50 mm (2 in.). Maximum length: 610 mm (24 in.).
4B150	Welded steel cylinder. Maximum service pressure 1035 kPa (150 psi).
4BA225	Welded steel cylinder. Steels definitely prescribed. Maximum service pressure 1550 kPa (225 psi).
4BW225	Welded steel cylinder. Steels definitely prescribed. Electric-arc welded longitudinal seam. Maximum service pressure 1550 kPa (225 psi).

* Canadian Transport Commission and Department of Transportation (U.S.)

The only opening permitted in the tank is a single manway located in the centre at the top. Four valves are mounted inside the dome cover similar in arrangement to ammonia tank car unloading arrangement. Three of these are angle valves; the fourth, mounted in the centre, is a safety relief valve. The two liquid angle valves are mounted on the centre line of the tank, while the single gas angle valve and a gauging device assembly are mounted on the transverse centre line (TCM 1979; PPH 1974). Occasionally, the positions of the relief valve and gauging devices are interchanged.

Under each liquid valve is an eduction pipe fastened to the manway cover and extending to the bottom of the tank. At the top of each eduction pipe, immediately below the manway cover, is a rising-ball, excess-flow valve designed to close when the rate of flow of liquid exceeds about 3180 kg/h (7000 lb./h). This is a protective device designed to close automatically against the flow of liquid if the angle valve is broken off or, under

TABLE 3 RAILWAY TANK CAR SPECIFICATIONS

CTC/DOT* Specification Number	Description
105A200W	Steel fusion-welded tank with manway nozzle. Insulated. Top unloading arrangement required. Test pressure 1380 kPa (200 psi). Bottom outlet or washout prohibited.
105A300W	As above except test pressure 2070 kPa (300 psi).
112A340W**	Steel fusion-welded tank with manway nozzle. Uninsulated. Upper 2/3 must be painted. Top unloading arrangement required. Test pressure 2340 kPa (340 psi). Bottom outlet or washout prohibited. Maximum one opening for purging tank interior.
114A340W**	Same as 112A340W but manway may be located other than at top of tank. Valves and fittings need not be mounted on manway cover.

* Canadian Transport Commission and Department of Transportation (U.S.)

** Note: Both 112A340W and 114A340W have been retrofitted with head shields and insulation and are now designated 112J340W, 112T340W or 112S340W (CCPA 1983).

certain conditions, if the unloading line is severed. The safety relief valve is of the spring-loaded type. A 19 mm (3/4 in.) thermometer well and a gauging device (magnetic, manual or electronic) are also required (TCM 1979; RTDCR 1974).

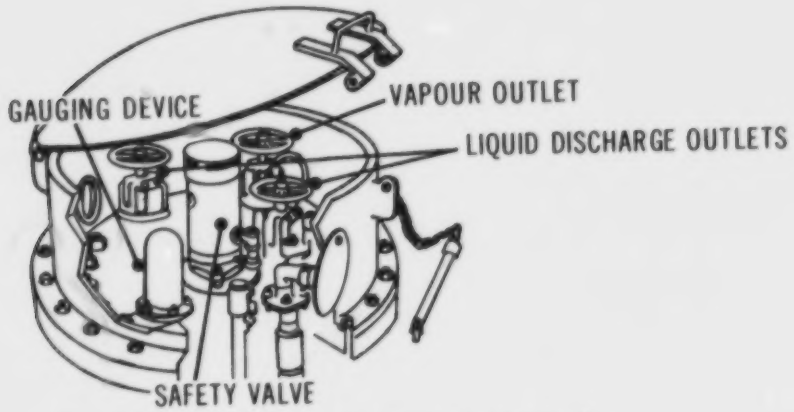
4.1.5 **Tank Motor Vehicles.** Vinyl chloride tank motor vehicles consist of a cargo tank pulled by a tractor. The maximum tank capacity is restricted by highway load limits. They must comply with Transport Canada Specification TC331 (DOT MC331) as outlined in Table 5 (MCA 1972). Most tanks have a capacity varying from 13.6 to 18.1 tonnes (15 to 20 tons). The minimum design pressure of these tanks is 1030 kPa (150 psi) (HCG 1981).

All tanks are provided with at least 13 mm (1/2 in.) of insulation protected by a steel jacket. The only tank opening permitted is a manway located at the top. The valve arrangement is the same as that on tank cars except that excess-flow valves are also required under the gas valves. The operating angle valves are the same as those on tank cars. Immediately below each liquid angle valve are an excess-flow valve and an

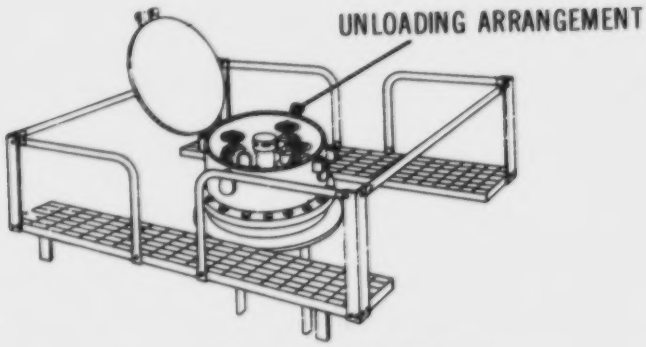
VINYL CHLORIDE

RAILWAY TANK CAR CLASS - CLASS 105A300W

Reference: TCM 1979; RTDCR 1974



Detail of top unloading arrangement



Detail of loading platform

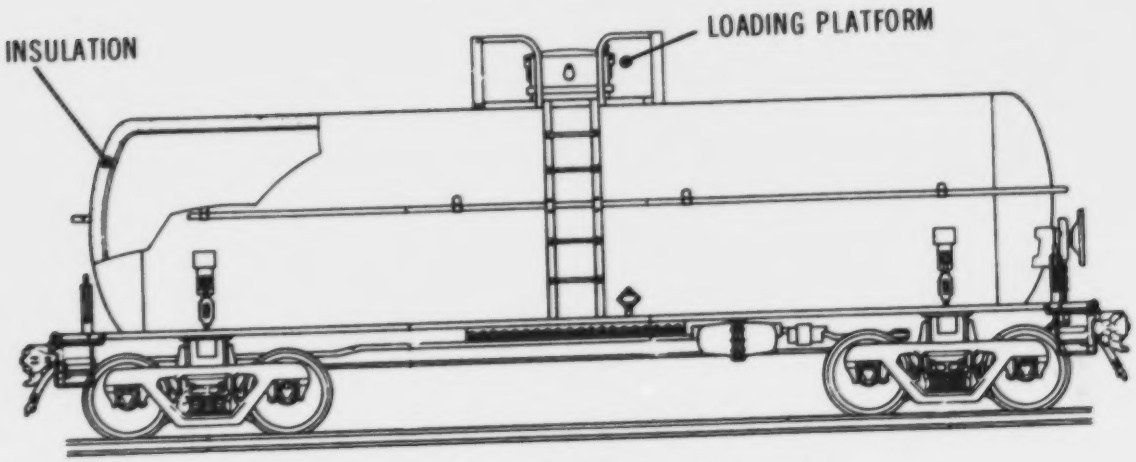


Illustration of tank car layout

TABLE 4 TYPICAL RAILWAY TANK CAR SPECIFICATIONS - CLASS 105A300W (TCM 1979; RTDCR 1974)

Description	Tank Car Size (Imp. Gal.) 9000	21 000	28 000
Overall			
Nominal capacity	41 000 L (9000 gal.)	95 000 L (21 000 gal.)	127 000 L (28 000 gal.)
Car weight - empty	30 300 kg (66 800 lb.)	40 800 kg (90 000 lb.)	50 800 kg (112 000 lb.)
Car weight - max.	80 300 kg (177 000 lb.)	83 500 kg (184 000 lb.)	119 000 kg (263 000 lb.)
Tank			
Material	Steel	Steel	Steel
Thickness	17.5 mm (11/16 in.)	17.5 mm (11/16 in.)	17.5 mm (11/16 in.)
Inside diameter	2.2 m (88 in.)	2.4 m (95 in.)	3.0 m (120 in.)
Test pressure	2070 kPa (300 psi)	2070 kPa (300 psi)	2070 kPa (300 psi)
Burst pressure	51 700 kPa (750 psi)	51 700 kPa (750 psi)	51 700 kPa (750 psi)
Valve release pressure	1550 kPa (225 psi)	1550 kPa (225 psi)	1550 kPa (225 psi)
Approximate Dimensions			
Coupled length	13 m (42 ft.)	20 m (65 ft.)	20 m (67 ft.)
Length over strikers	12 m (40 ft.)	19 m (63 ft.)	20 m (64 ft.)
Length of truck centres	9 m (29 ft.)	16 m (52 ft.)	16 m (53 ft.)
Height to top of grating	4 m (12 ft.)	4 m (12 ft.)	4 m (12 ft.)
Overall height	5 m (15 ft.)	5 m (15 ft.)	5 m (15 ft.)
Overall width	3.2 m (127 in.)	3.2 m (127 in.)	3.2 m (127 in.)
Length of grating	2-3 m (7-10 ft.)	2-3 m (7-10 ft.)	2-3 m (7-10 ft.)
Width of grating	1.5-2 m (5-6 ft.)	1.5-2 m (5-6 ft.)	1.5-2 m (5-6 ft.)
Loading/Unloading Fixtures			
Unloading connections/ Valving	Two 76 mm (3 in.) valves to liquid, via check valve; one 51 mm (2 in.) valve to vapour space via check valve		
Safety Devices	Safety relief valve set at 1550 kPa (225 psi)		
Insulation	102 mm (4 in.) foam or cork insulation		

TABLE 5 TANK MOTOR VEHICLE SPECIFICATIONS

TC* Specification Number	Description
TC331 (or MC331)	Seamless or welded steel tank. Design and construct in accordance with ASME Code. One opening with protective housing and manway cover. Maximum design pressure 3450 kPa (500 psi). Insulated. Postweld heat treatment as per ASME Code. Gauging device prohibited. Minimum design pressure 1030 kPa (150 psi).

* Transport Canada

eduction pipe the same as those on tank cars. In addition, under each gas valve there is an excess-flow valve of different design, to prevent outward flow of gas if the angle valve is broken off. The safety relief valve is of the spring-loaded type.

4.2 Off-loading

4.2.1 Off-loading Equipment and Procedures for Cylinders and Ton Containers. Both cylinders and ton containers are handled and stored in the same manner. The following points should be observed when handling and storing containers (MCA 1972):

- Valve protection hoods should be in place.
- Containers should not be stored near ventilating systems.
- Store to minimize external corrosion.
- Store cylinders upright, ton containers on their sides.
- Store full and empty containers separately.

Cylinders deliver vinyl chloride gas when in an upright position and liquid when in an inverted position. Ton containers, when in a horizontal position and with the valves in a vertical line, deliver gas from the upper valve and liquid from the lower valve.

A check valve should be installed in feed lines when using cylinders or ton containers, to prevent the reactants from entering the container (MCA 1972).

4.2.2 Off-loading Equipment and Procedures for Railway Tank Cars and Tank Motor Vehicles. Railway tank cars and tank motor vehicles are basically off-loaded in the same manner but only after the following precautionary items have been undertaken (MCA 1972; VCM 1982):

- Unloading operations to be performed only by properly instructed personnel.
- Rail cars, tracks, loading platforms, etc., are grounded and piping is bonded and grounded.
- Dead-end siding used only for vinyl chloride rail cars to be provided.
- Brakes must be set, wheels chocked, proper derails employed, and caution placards displayed.
- Suitable operating platform to be provided at unloading point.

The railway tank car or highway vehicle may be unloaded by pumping or by inert gas (MCA 1972). When using the pumping method, liquid is pumped from one of the two liquid angle valves. When gas is required, discharge vinyl chloride gas from the gas angle valve.

When using the inert gas method, dry inert gas (usually nitrogen) is used to increase car pressure. Larger unloading installations may have a suction line connected from the storage tank to a compressor which discharges compressed vinyl chloride gas to the tank car (MCA 1972; VCM 1982). The pressure on the car should never exceed the service pressure at which the safety valve is set to operate.

After unloading lines have been disconnected, valve outlet plugs should be immediately replaced to prevent thread corrosion. After unloading, leave at least 70 kPa (10 psi) vinyl chloride, to prevent the ingress of air, and mark the tank as "empty - flammable gas" (VCM 1982).

4.2.3 Specifications and Materials for Off-loading Equipment. Under this section, the components of a typical off-loading system handling dry vinyl chloride at commonly employed temperatures and pressures will be discussed. These include pipes and fittings, valves, gaskets, pumps and storage tanks.

Pipes and fittings should be of Schedule 80 seamless carbon steel designed to have a working pressure of at least 690-1035 kPa (100-150 psi), with a safety factor conforming to the ASME (MCA 1972). Pipeline joints should preferably be flanged or welded. If threaded joints are necessary, extreme care must be taken to obtain clean, sharp pipe threads, in order to ensure pressure-tight joints. These should be back welded to ensure that there is no leakage and that there is good grounding (CCPA 1983).

Steel plug valves are in common use (CCPA 1983). Cast steel diaphragm valves lined with chlorinated polyether resin will serve adequately (DPLV 1972). Valves and fittings should not be of cast iron as these can easily crack (VCM 1982). Viton may be used as a gasket material at normal operating temperatures.

A jacketed sealless magnetic drive centrifugal pump with "wet end" material of carbon steel gives good results. Chilled refrigerant should be fed to the jacketing to keep the pumpage below the boiling point and thus prevent vaporization. Leakage from this type of pump should be virtually eliminated. The pump must be provided with a drain so that repairs can be safely made.

Storage tanks should be of all-welded steel construction and grounded (MCA 1972).

4.3 Compatibility with Materials of Construction

The compatibility of vinyl chloride with materials of construction is indicated in Table 6. The unbracketed abbreviations are described in Table 7. The rating system for this report is briefly described below.

Recommended: This material will perform satisfactorily in the given application.

Conditional: Material will show deterioration in the given application; however, it may be suitable for intermittent or short-term service.

Not Recommended: Material will be severely affected in this application and should not be used.

TABLE 6 COMPATIBILITY WITH MATERIALS OF CONSTRUCTION

		Material of Construction		
Application	Temp. (°C)	Recommended	Conditional	Not Recommended
1. Pipes and Fittings	24	PVDF Chlorinated Polyether (DCRG 1978)		PVDC (DCRG 1978)
	Most	CS CI (MCA 1972) SS (VCM 1982)	CI (VCM 1982)	
2. Valves	Normal	CS CI (MCA 1972) SS (VCM 1982)	CI (VCM 1982)	Copper (MCA 1972)

TABLE 6 COMPATIBILITY WITH MATERIALS OF CONSTRUCTION (Cont'd)

		Material of Construction		
Application	Temp. (°C)	Recommended	Conditional	Not Recommended
3. Storage	Normal	CS CI (MCA 1972)	CI (VCM 1982)	Aluminum (VCM 1982)
4. Others	24–100	Glass (CDS 1967)		Copper Brass (VCM 1982)

TABLE 7 MATERIALS OF CONSTRUCTION

Abbreviation	Material of Construction
	Chlorinated Polyether
CI	Cast Iron, Austenitic
CS	Carbon Steel
	Fluorine Rubber (Viton)
	Glass
PVDC	Polyvinylidene Chloride
PVDF	Polyvinylidene Fluoride
SS	Stainless Steel

5 CONTAMINANT TRANSPORT

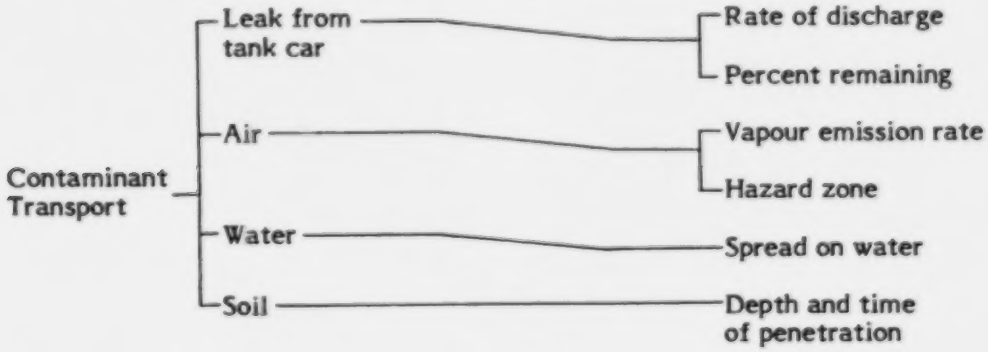
5.1 General Summary

Vinyl chloride is commonly transported in tanks as a liquefied compressed gas. When spilled in the environment, it will form a liquid pool, spreading on the surface of a water body or on the ground as well as forming a visible vapour cloud. Vapour is released rapidly from the pool to the atmosphere by evaporation. The initial release will result in a large release of vapour (puff). As the vinyl chloride cools as a result of the evaporation, the vapour release will slow. If the ambient temperature is low, e.g., below the boiling point of -13.4°C, little evaporation may occur.

When spilled on water, some of the material will dissolve, and the rest will evaporate to the atmosphere. The vapour cloud tends to hug the water and spread rather than lifting off the surface and dispersing.

Vinyl chloride spills on soil surfaces will partly vaporize, and partly adsorb onto the soil at a rate dependent on the soil type and its degree of saturation with water. Downward transport of the liquid toward the groundwater table may cause environmental concerns.

The following factors are considered for the transport of a vinyl chloride spill in the air, water and soil media:



It is important to note that, because of the approximate nature of the contaminant transport calculations, the approach adopted throughout has been to use conservative estimates of critical parameters so that predictions are approaching worst case scenarios for each medium. This may require that the assumptions made for each medium be quite different and to some extent inconsistent. As well as producing worst case scenarios, this approach allows comparison of the behaviours of different chemicals under consistent assumptions.

5.2 Leak Nomograms

5.2.1 Introduction. Vinyl chloride is commonly transported as a liquefied compressed gas at ambient temperature. While the capacities of the railway tank cars vary widely, one size has been chosen throughout the EnviroTIPS series for development of the leak nomograms. It is approximately 2.75 m in diameter and 13.4 m long, with a carrying capacity of about 80 000 L.

If a tank car loaded with liquefied vinyl chloride is punctured on the bottom, all of the contents will drain out. The instantaneous discharge rate (q) is a function of the height of the fluid above the hole (H), the internal pressure of the tank (P), the hole size (A) and shape, and a coefficient of discharge (C_d). For the purposes of nomogram preparation, a constant discharge coefficient of 0.8 has been assumed.

If the tank car is punctured in the top or at any point above the liquid level, gas will be vented until all of the liquid has vaporized and the internal and external tank pressures have equalized. For the purposes of nomogram preparation, the liquid is assumed to remain at a constant temperature (isothermal) equal to the ambient temperature (T). Consequently, the venting rate (q) is assumed to be constant until all of the liquid is vaporized. The venting rate is a function of the internal tank pressure (P), which is equal to the saturated vapour pressure (P_{sat}) of the liquid at temperature T. The assumed maximum tank ambient temperature is 40°C, yielding a saturated vapour pressure (P_{sat}) of 600 kPa.

The assumption of isothermal conditions will maximize the gas release rate from the tank and will be conservative for most cases. In reality, however, the boiling point of vinyl chloride is within Canadian environmental conditions (-13.4°C) and thus the vapour emission from a puncture above the liquid level will be substantially less than predicted here. After the puncture, the vapour will be released rapidly; probably as a puff; evaporative cooling will substantially reduce subsequent emissions. It is estimated that the vapour emission rate would be about 1 order of magnitude lower than that predicted here if the car has lost some of its insulation and the ambient temperature is 10-30°C. The rate predicted here will be true if the car has lost a substantial portion of its insulation and the ambient temperature is 40°C or above. The vapour emission rate could be 3 or 4 orders of magnitude slower than predicted here if the ambient temperature is near the boiling point.

The aim of the nomograms is to provide a simple means to obtain the time history of the venting process. This may include venting from a bottom puncture (liquid

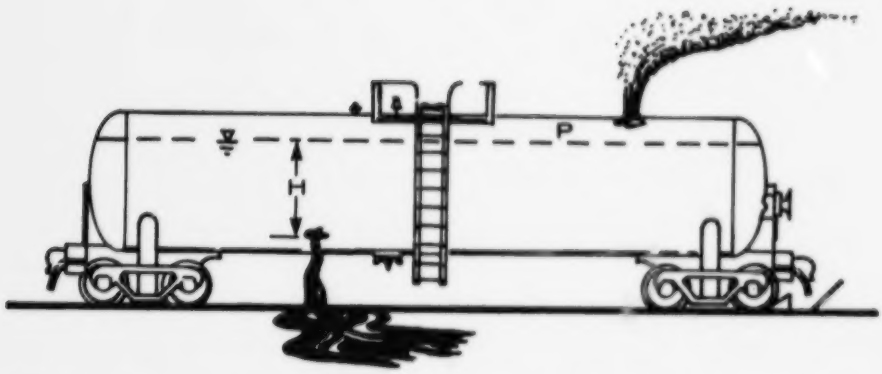


FIGURE 7 TANK CAR WITH PUNCTURE HOLE IN BOTTOM OR TOP

release) or from a puncture above the liquid level (gas venting). The details of the models used to calculate venting rates are described in the Introduction Manual.

5.2.2 Nomograms.

5.2.2.1 Bottom puncture - liquid venting.

Figure 8: Percent remaining versus time. Figure 8 provides a means of estimating the percent of vinyl chloride remaining in the standard tank car after the time of puncture for a number of different hole diameters. The hole diameter is actually an equivalent diameter and can be applied to a noncircular puncture.

The standard tank car is assumed to be initially full (at t=0) with a volume of about 80 000 L of vinyl chloride at 40°C. The amount remaining at any time (t) is not only a function of the discharge rate over time, but also of the size and shape of the tank car.

Figure 9: Discharge rate versus puncture size. Figure 9 provides a means of estimating the maximum discharge rate (L/s) for a number of equivalent hole diameters. As the pressure force dominates the gravitational force, the discharge rate remains relatively constant as the tank empties.

5.2.2.2 Top puncture - gas venting.

Figure 10: Percent remaining versus time. Figure 10 provides a means of estimating the percent of vinyl chloride remaining in the standard tank car after the time of puncture for a number of different hole diameters. The hole diameter is actually an equivalent diameter and can be applied to a noncircular puncture. As isothermal conditions have been assumed, the internal pressure and venting rate are constant.

FIGURE 8

VINYL CHLORIDE

PERCENT REMAINING vs TIME

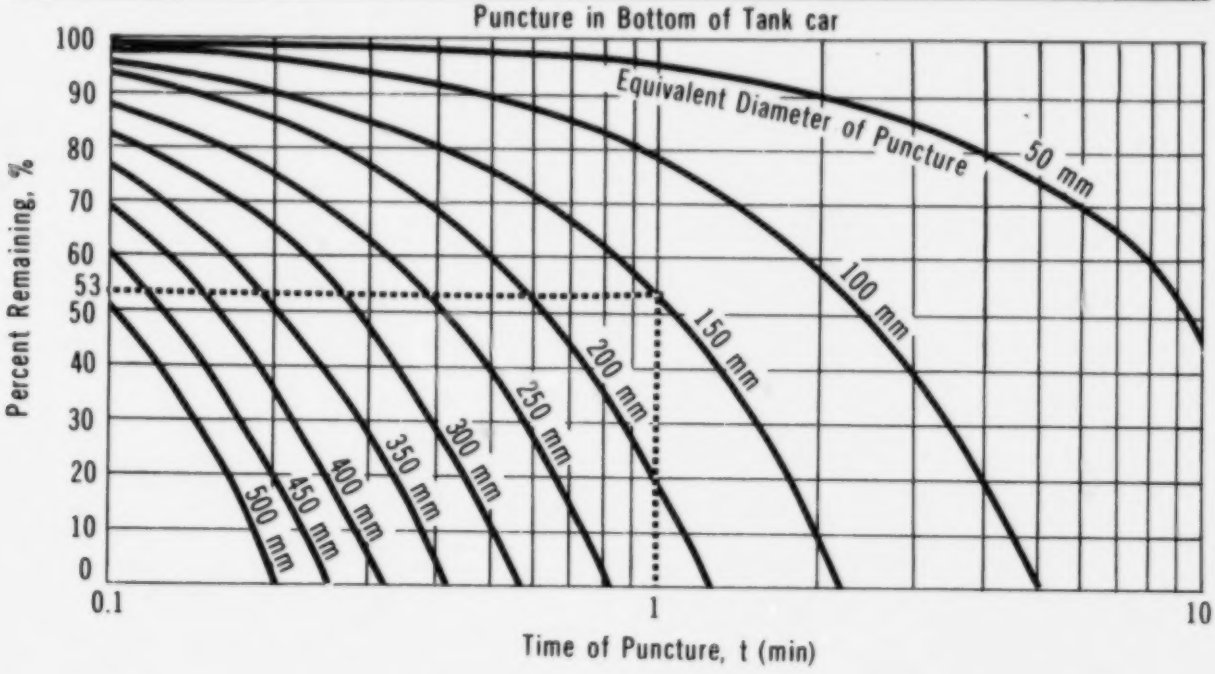


FIGURE 9

VINYL CHLORIDE

DISCHARGE RATE vs PUNCTURE SIZE

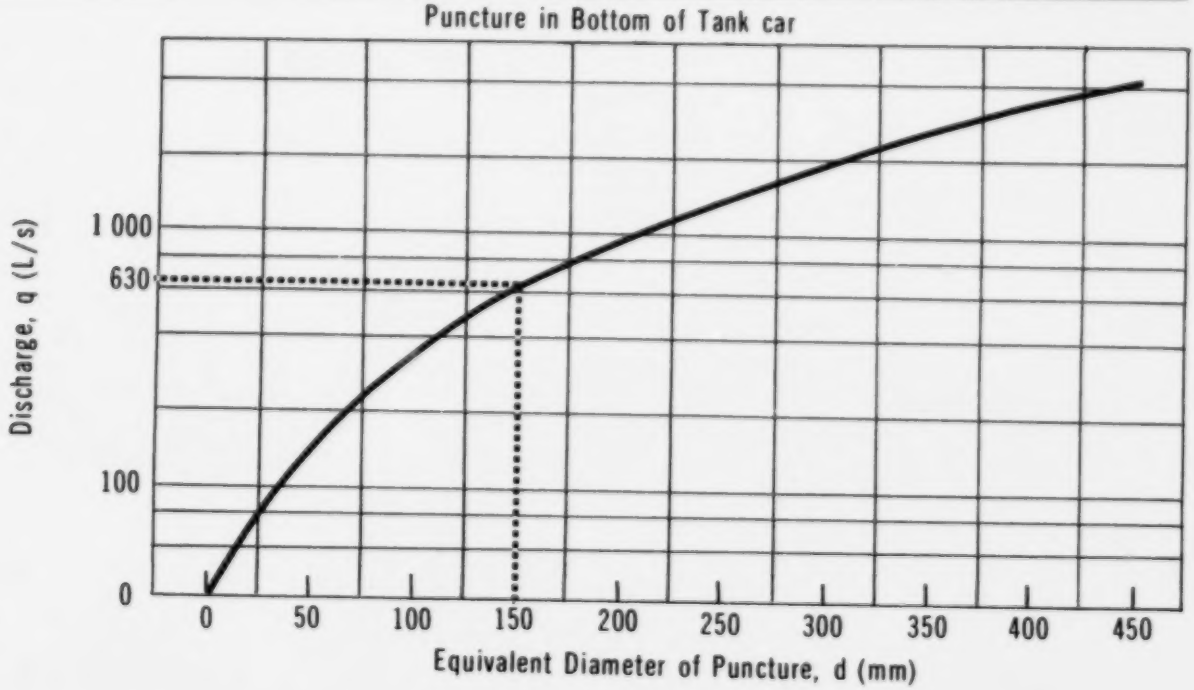


FIGURE 10

VINYL CHLORIDE

PERCENT REMAINING vs TIME

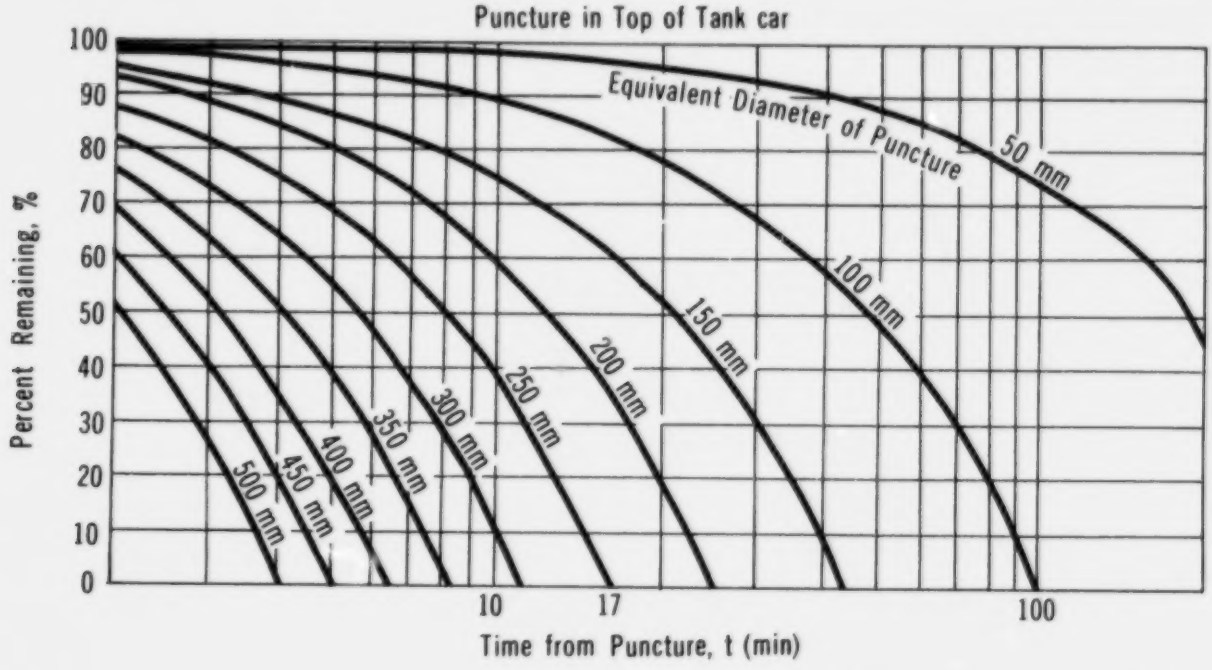


FIGURE 11

VINYL CHLORIDE

DISCHARGE RATE vs PUNCTURE SIZE

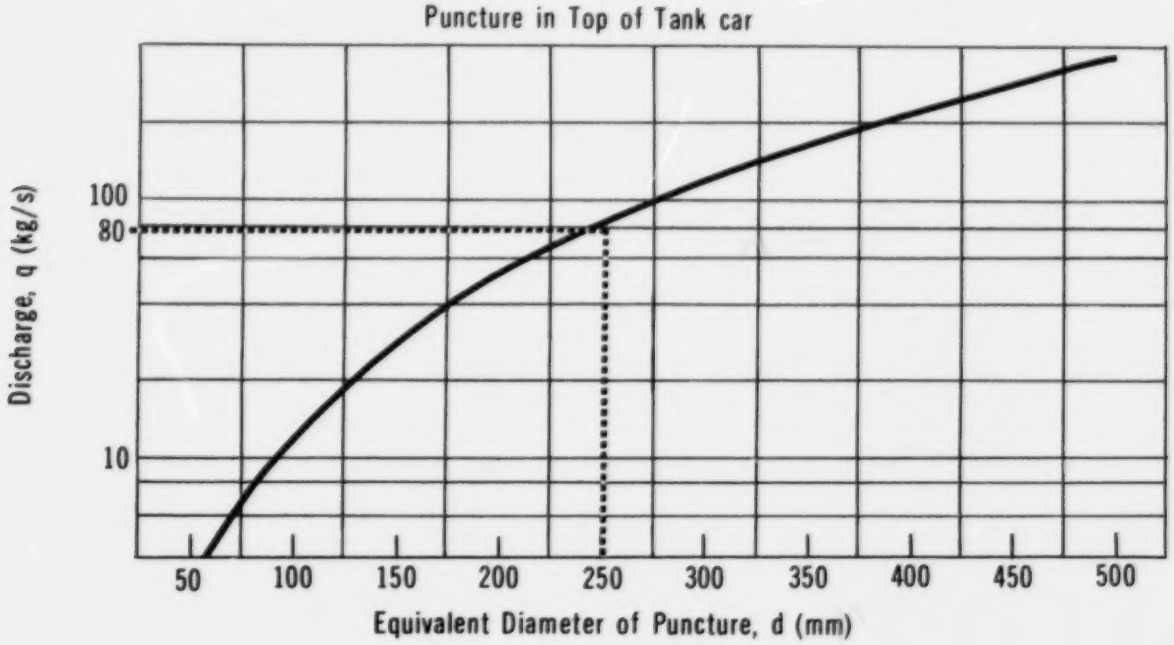


Figure 11: Discharge rate versus puncture size. Figure 11 presents the relationship between discharge rate (kg/s) and the equivalent diameter of the hole for gas venting above the liquid level in the tank car. For any one hole size, the venting rate will be constant until all the liquid is vaporized. This is consistent with the assumption of isothermal conditions in the tank and results in a conservative estimate of the gas venting rate.

The values presented in Figure 11 are independent of the tank car size, but assume that the temperature of the liquid is 40°C, yielding a saturated vapour pressure of 600 kPa.

5.2.3 Sample Calculations.

i) Problem A

The standard tank car filled with vinyl chloride 40°C has been punctured on the bottom. The equivalent diameter of the hole is 150 mm. What percent of the initial 80 000 L remains after 1 minute and what is the instantaneous discharge rate from the tank?

Solution to Problem A

Step 1: Calculate the amount remaining at t=1 min

- Use Figure 8
- With t=1 min and d=150 mm, the amount remaining is about 53 percent or 42 000 L

Step 2: Calculate the discharge rate

- Use Figure 9
- With d=150 mm, the instantaneous discharge rate (q) = 630 L/s

ii) Problem B

The standard tank car in Problem A has been punctured above the liquid level. The equivalent diameter of the orifice is estimated at 250 mm. How long will it take to empty the tank car and what is the release rate, assuming isothermal conditions?

Solution to Problem B

Step 1: Calculate the time to empty

- Use Figure 10

- With d=250 mm, the tank empties (0 percent remaining) in approximately 17 min

Step 2: Calculate the discharge rate

- Use Figure 11
- With d=250 mm and assuming isothermal conditions, the venting rate is constant at 80 kg/s. As noted above, this will be the most rapid discharge rate in normal circumstances; depending on ambient temperatures, insulation, etc., the rate could be up to 4 orders of magnitude slower.

5.3 Dispersion in the Air

5.3.1 Introduction. Since vinyl chloride under pressure is an extremely volatile liquid, vapour released from a liquid pool spilled on a ground or water surface vaporizes rapidly enough to consider the spill as producing instantaneous vapour in the form of a puff. Only this type of vapour release is treated here. As noted above, the evaporation rate after the puff is released would be slow and depends on ambient temperatures.

To estimate the vapour concentrations downwind of the accident site for the determination of the flammability or toxicity hazard zone, the atmospheric transport and dispersion of the contaminant vapour must be modelled. The models used here are based on Gaussian formulations and are the ones most widely used in practice for contaminant concentration predictions. The model details are contained in the Introduction Manual.

Figure 12 depicts schematically the contaminant puff configuration from a surface release. The dispersion model represents the spill as an instantaneous point source (with a total vapour release quantity, Q_T) equal to the amount of contaminant spilled.

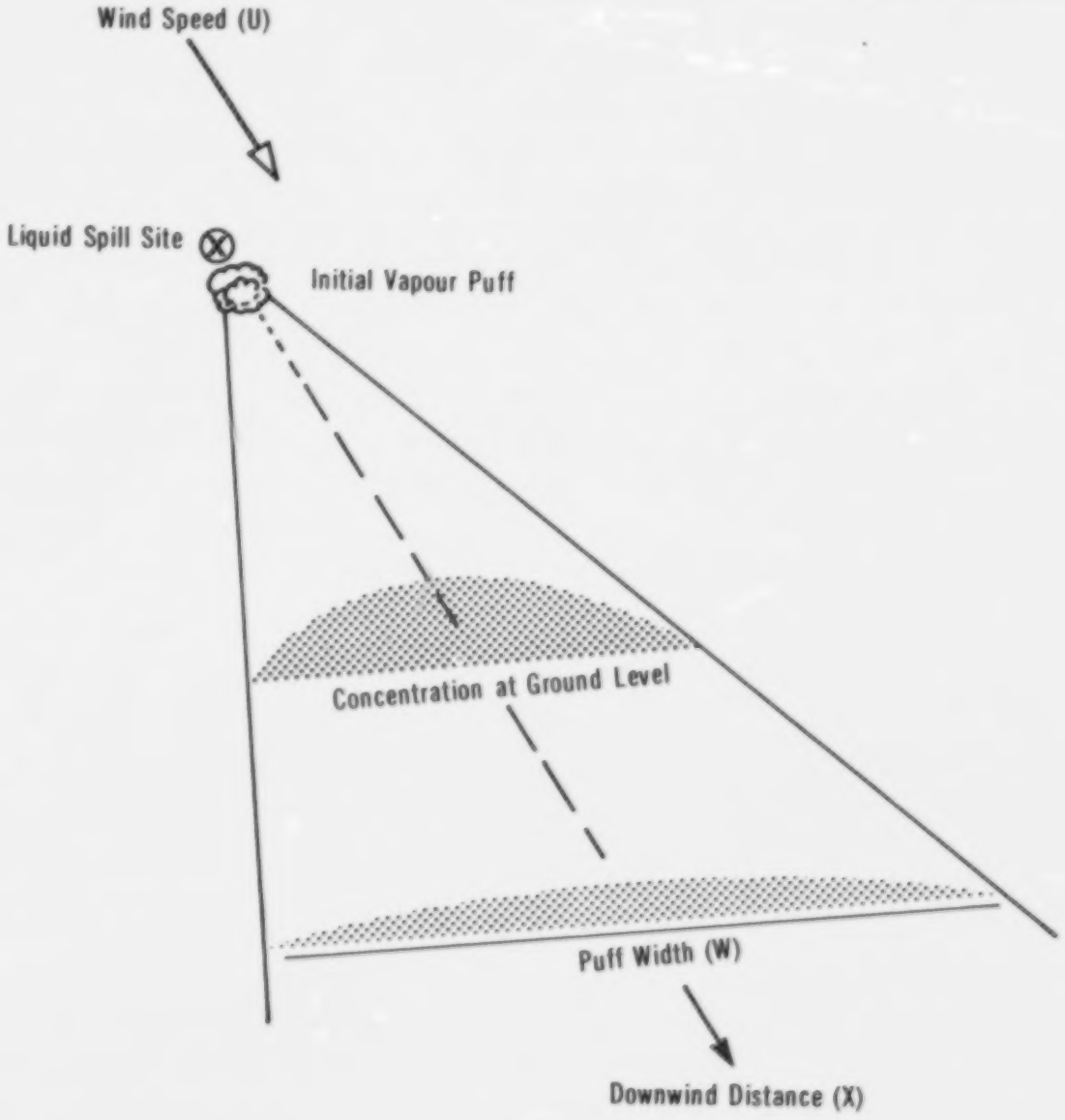
Although no relevant spill information is available on the behaviour of a cloud of vinyl chloride gas, it is expected that in the initial period immediately after the spill, the cloud will behave as a denser-than-air gas. This is due primarily to the greater density of vinyl chloride gas (2.2 times that of air at 20°C) and due to the fact that the vapour cloud arising from the cold bulk liquid will be cold itself. Ground hugging and gas accumulation in low-lying areas may therefore be observed during the initial period. Conventional Gaussian modelling will tend to depict heavier-than-air plumes (puffs) to be narrower than observed.

Since the boiling point of liquid vinyl chloride is low for a liquefied gas (-14°C at 1 atm), spills on a ground surface at very low temperatures (-15°C and less) will result

FIGURE 12

VINYL CHLORIDE

SCHEMATIC OF CONTAMINANT PUFF



in considerable overestimation since the vapour emission rate would not approach that of a puff release situation and worst case values would be provided. Based on published information pertaining to spills of vinyl chloride at low air temperatures (-19°C) onto snow-covered terrain (Fraser 1981), the use of the puff modelling method will greatly overestimate the hazard since only about 2.5 percent of instantaneously released vinyl chloride boiled off rapidly. For spills occurring at air temperatures of about 20°C and greater, the puff modelling scenario will be more appropriate and more realistic results will be calculated. For these reasons it will be assumed that only 25 percent of the instantaneously spilled vinyl chloride will produce an instantaneous vapour puff. It is recognized that although 75 percent of the vinyl chloride remains and poses a potential source of hazard, the vapour emission rate will be small in comparison to the initial puff release. Also, the hazard zone determined for the initial puff release will provide conservative estimates.

5.3.2 Vapour Dispersion Nomograms and Tables. The aim of the air dispersion nomograms is to define the hazard zone due to toxicity or flammability of a vapour cloud. The following nomograms and data tables are contained in this section (to be used in the order given):

Table 8:	weather conditions
Figure 14:	normalized vapour concentration as a function of downwind distance
Table 9:	maximum puff hazard half-widths
Figure 17:	puff travel time versus travel distance

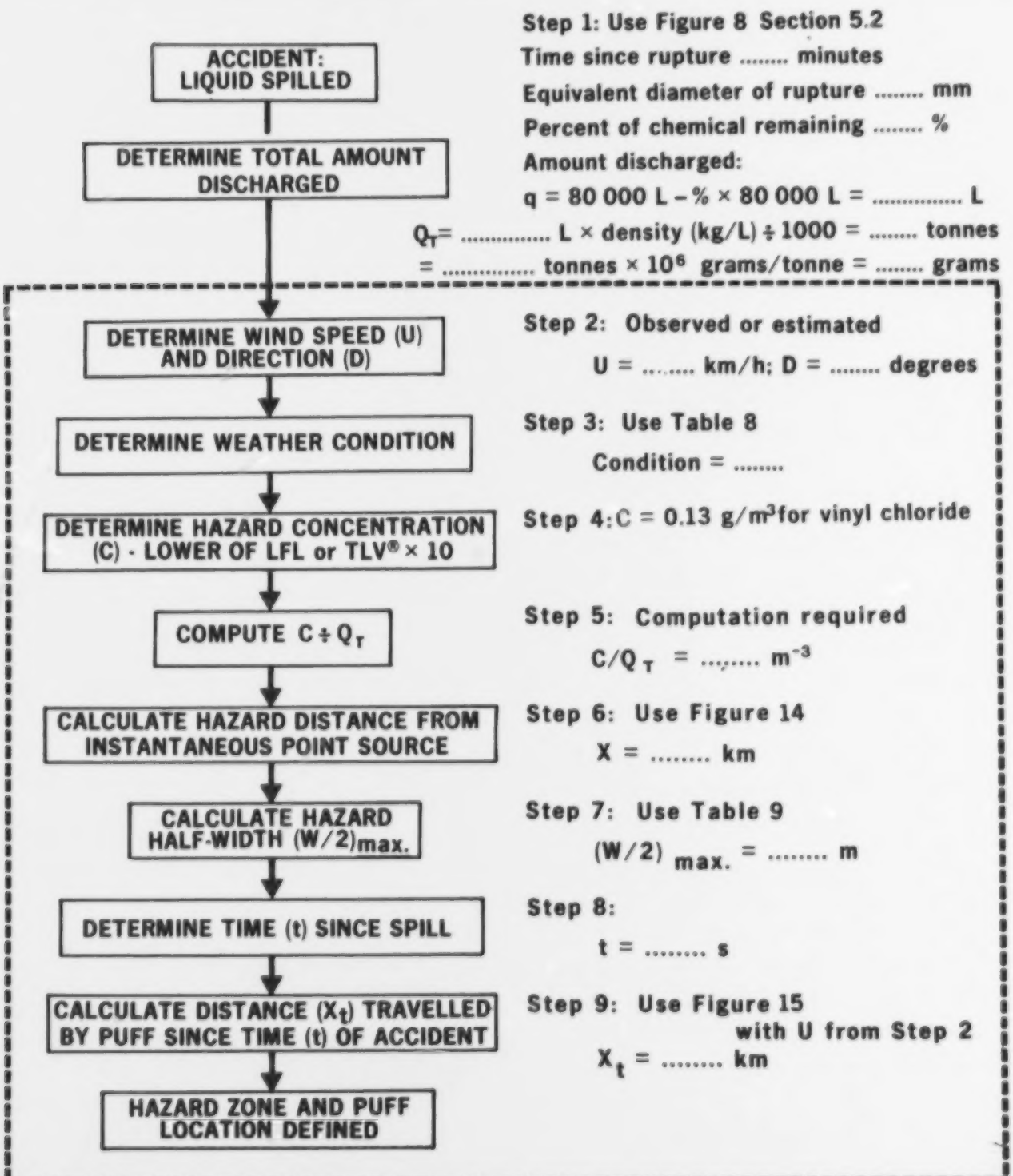
The flowchart given in Figure 13 outlines the steps necessary to make vapour dispersion calculations and identifies the nomograms or tables to be used. This section deals only with the portion contained within the dashed box. Data on "total liquid discharged" is contained in Section 5.2. A description of each vapour dispersion nomogram and its use follows.

5.3.2.1 Figure 14: Normalized vapour concentration versus downwind distance. Figure 14 shows the relationship between the vapour concentration and the downwind distance for weather conditions D and F. The nomograms were developed using the dispersion models described in the Introduction Manual. The vapour concentration is represented by the normalized, ground-level concentration (C/Q_T) at the centreline of the contaminant puff. Weather condition F is the poorest for dispersing a vapour cloud and

FIGURE 13

VINYL CHLORIDE

FLOW CHART TO DETERMINE VAPOUR HAZARD ZONE


ACCIDENT: LIQUID SPILLED
DETERMINE TOTAL AMOUNT DISCHARGED
DETERMINE WIND SPEED (U) AND DIRECTION (D)
DETERMINE WEATHER CONDITION
DETERMINE HAZARD CONCENTRATION (C) - LOWER OF LFL or TLV® × 10
COMPUTE C ÷ Q_T
CALCULATE HAZARD DISTANCE FROM INSTANTANEOUS POINT SOURCE
CALCULATE HAZARD HALF-WIDTH $(W/2)_{max.}$
DETERMINE TIME (t) SINCE SPILL
CALCULATE DISTANCE (X_t) TRAVELLED BY PUFF SINCE TIME (t) OF ACCIDENT
HAZARD ZONE AND PUFF LOCATION DEFINED
Step 1: Use Figure 8 Section 5.2
Time since rupture ..... minutes
Equivalent diameter of rupture ..... mm
Percent of chemical remaining ..... %
Amount discharged:
q = 80 000 L – % × 80 000 L = ... L
Q_T = ... L × density (kg/L) ÷ 1000 = ... tonnes
= ..... tonnes × 10^6 grams/tonne = ... grams
Step 2: Observed or estimated
U = ... km/h; D = ... degrees
Step 3: Use Table 8
Condition = ...
Step 4: C = 0.13 g/m³ for vinyl chloride
Step 5: Computation required
C/Q_T = ... m^{-3}
Step 6: Use Figure 14
X = ... km
Step 7: Use Table 9
$(W/2)_{max.}$ = ... m
Step 8:
t = ... s
Step 9: Use Figure 15
with U from Step 2
X_t = ... km

condition D is the most common in most parts of Canada. Before using Figure 14, the weather condition must be determined from Table 8.

TABLE 8 WEATHER CONDITIONS

Weather Condition F	Weather Condition D
Wind speed <11 km/h (≈3 m/s) and one of the following: - overcast day - night time - severe temperature inversion	Most other weather conditions

Use: The maximum hazard distance, X, downwind of the spill can be calculated from Figure 14 knowing:

- Q_T, the mass of vapour emitted (assumed equivalent to 25 percent of liquid spilled)
- U, the wind speed (m/s)
- the weather condition
- the hazard concentration limit, C, which is the lower value of 10 times the Threshold Limit Value (TLV®, in g/m^3), or the Lower Flammability Limit (LFL, in g/m^3). Note: To convert the TLV®, in ppm, and the LFL, in percent by volume, to concentrations in g/m^3, use Figures 15 and 16

A hazard concentration limit of 10 times the TLV® has been arbitrarily chosen as it represents a more realistic level at which there would be concern for human health on the short term (i.e., on the order of 30 minutes). The TLV® is a workplace standard for long-term exposure and use of this value as the hazard limit would result in unrealistically large hazard zones.

5.3.2.2 Table 9: Maximum puff hazard half-widths. This table presents data on the maximum puff hazard half-width, $(W/2)_{max}$, for a range of Q_T values under weather conditions D and F. These data were computed using the dispersion modelling techniques given in the Introduction Manual for a value of 10 times the vinyl chloride Threshold Limit Value (TLV®) of 0.013 g/m^3, or 0.13 g/m^3. The maximum puff hazard half-width represents the maximum half-width of the vinyl chloride vapour cloud, downwind of the spill site, corresponding to a hazard concentration limit of 10 x TLV®. Table 9 is

FIGURE 14

VINYL CHLORIDE

NORMALIZED VAPOUR CONCENTRATION VS DOWNWIND DISTANCE

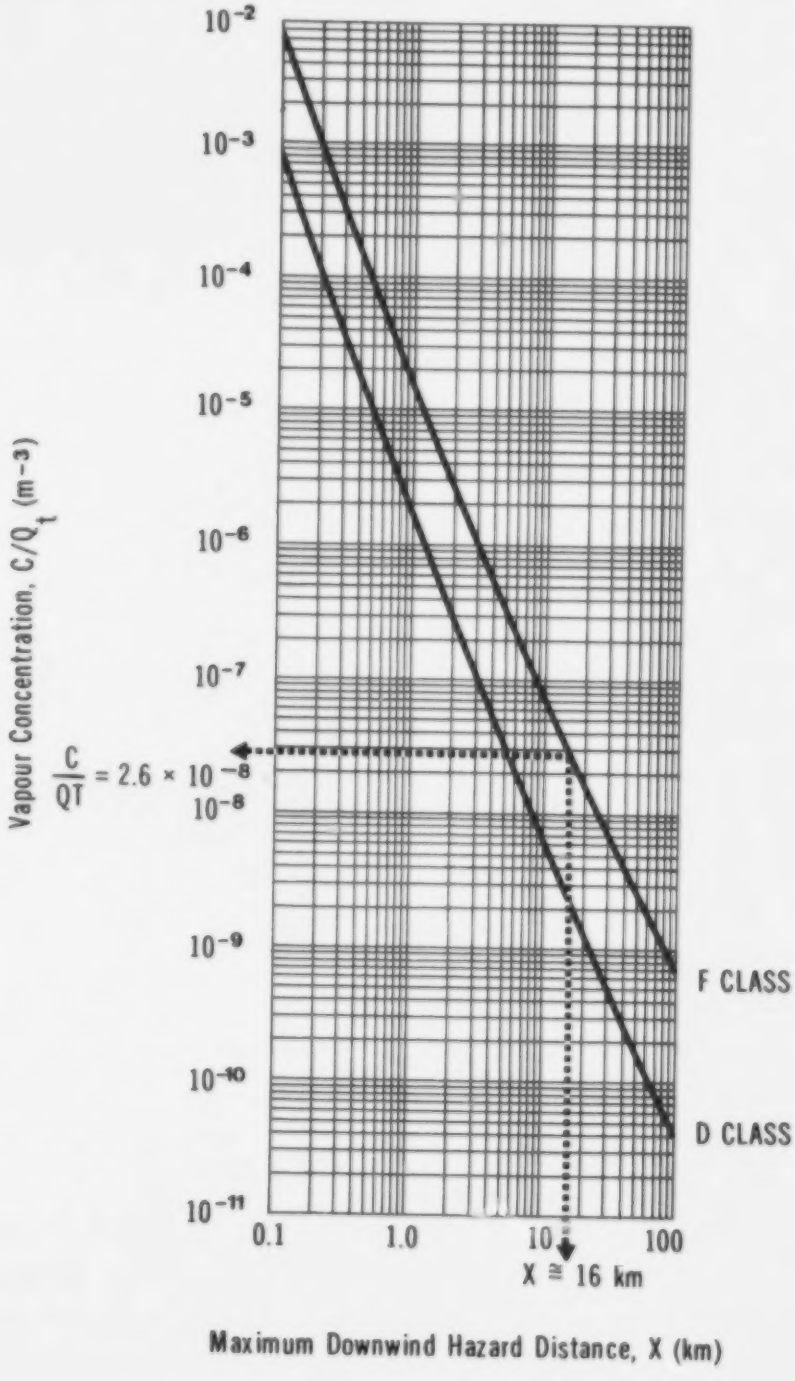


FIGURE 15

VINYL CHLORIDE

PUFF TRAVEL TIME VS TRAVEL DISTANCE

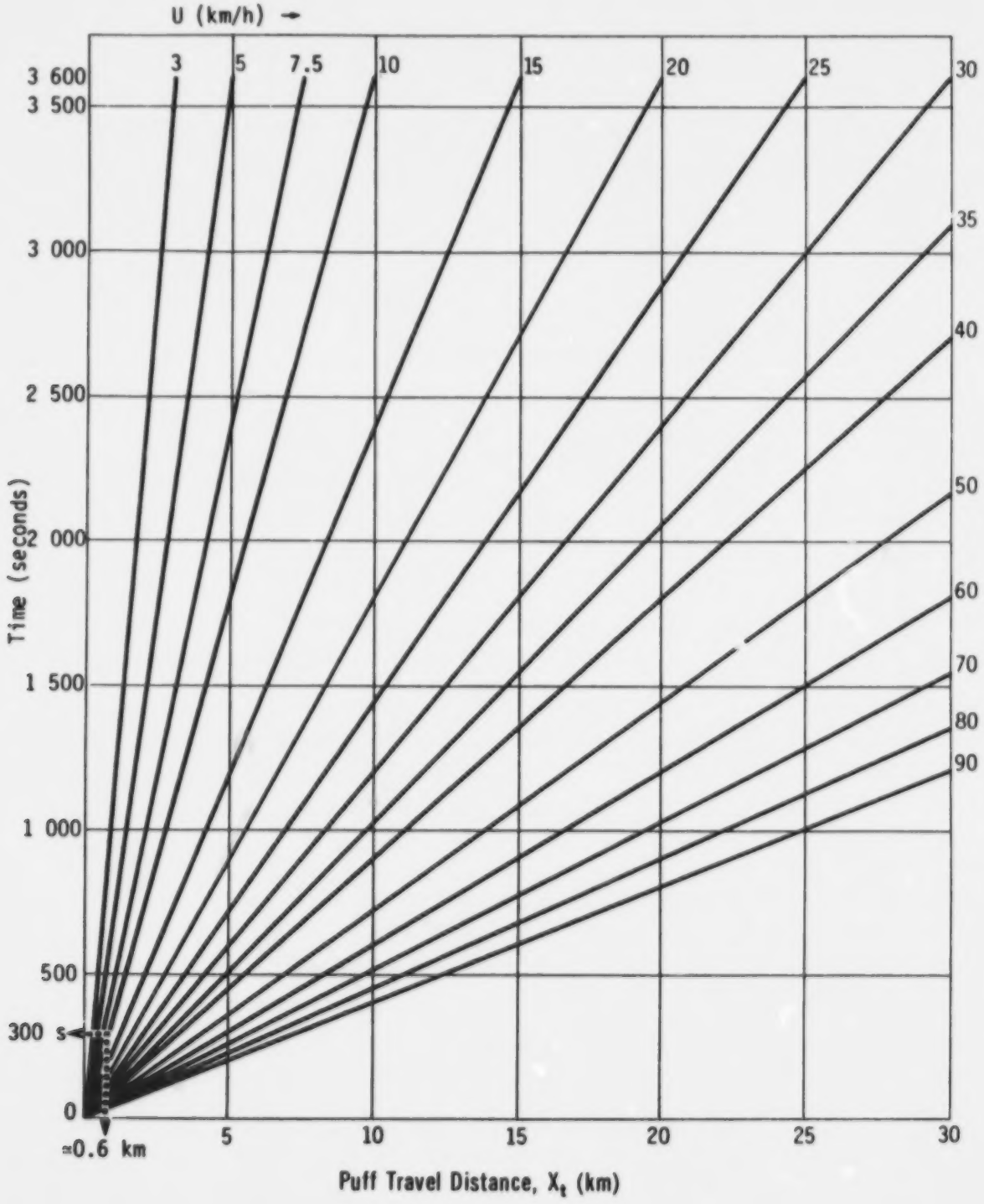
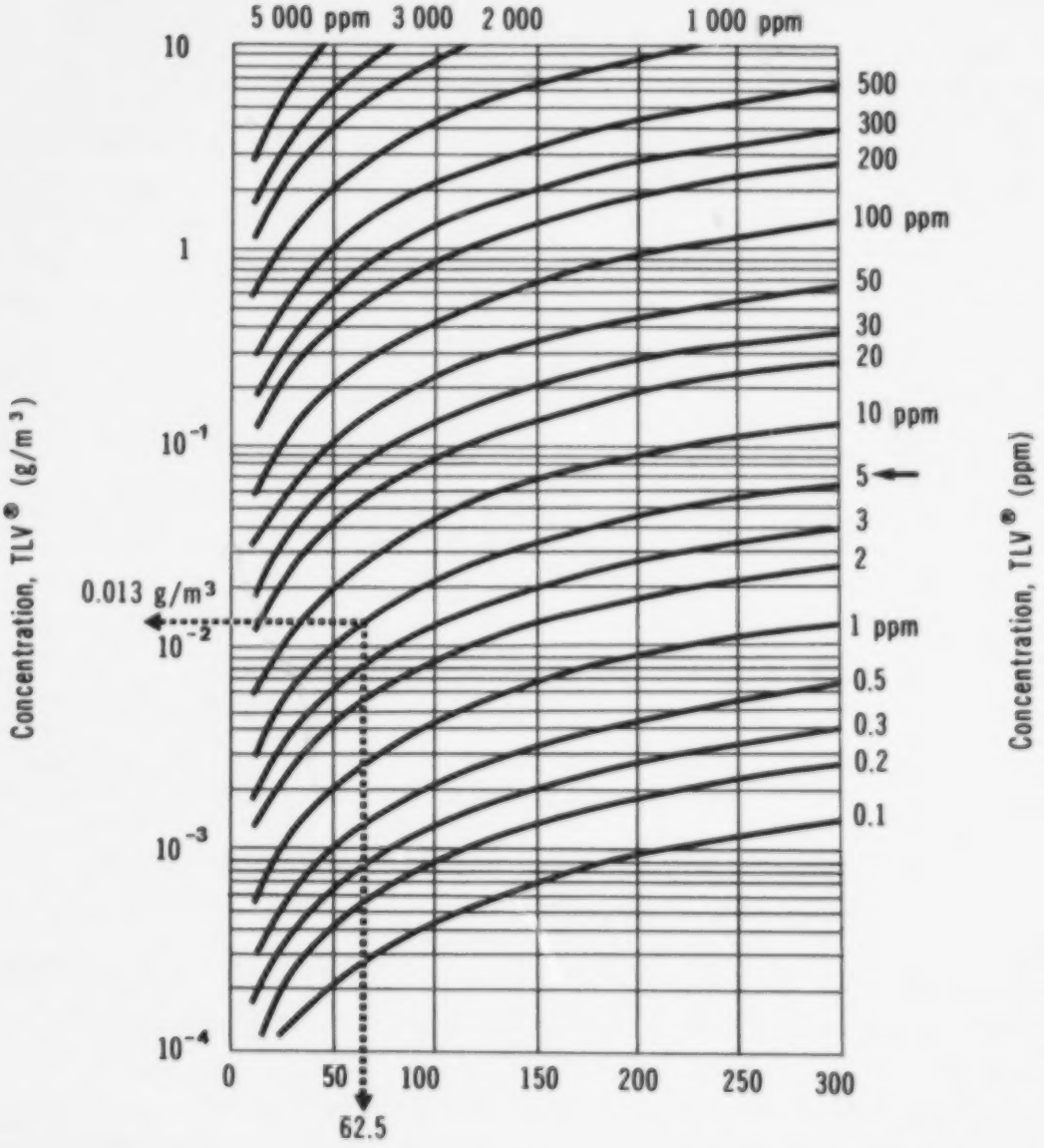


FIGURE 16

VINYL CHLORIDE

CONVERSION OF THRESHOLD LIMIT VALUE (TLV®) UNITS (ppm to g/m³)



Example: Vinyl Chloride, MW = 62.5, TLV® = 5 ppm,
then TLV® in g/m³ = 0.013

Note: data applicable at 25°C and 760 mm Hg pressure

TABLE 9 MAXIMUM PUFF HAZARD HALF-WIDTHS (FOR VINYL CHLORIDE)

Weather Condition D			Weather Condition F		
Q/T (tonnes)	$(W/2)_{max}$ (m)		Q/T (tonnes)	$(W/2)_{max}$ (m)	
4100	3995	(98.6 km)*	190	1840	(98.2 km)*
4000	3960		175	1780	
3000	3550		150	1665	
2000	3040		125	1540	
1000	2330		100	1400	
800	2140		75	1240	
600	1920		50	1040	
400	1640		40	945	
300	1470		30	835	
200	1260		25	775	
150	1130		20	705	
100	970		10	525	
75	865		7.5	460	
50	740	Q/T = 5 tonnes →	5	395 →	$(W/2)_{max}$ = 395 m
25	580		2.5	300	
20	535		1	210	
10	415		0.5	160	
7.5	370		0.1	80	
5	320		0.05	65	
2.5	250		0.01	40	
1	175				
0.5	135				
0.1	75				
0.05	60		* Data are provided up to a maximum downwind hazard distance of 100 km.		
0.01	35				

Example: Under weather condition F and Q/T = 5 tonnes, the puff hazard half-width $(W/2)_{max}$ = 395 m

Note: Above table is valid only for a vinyl chloride concentration of 10 x TLV●, or 0.13 g/m^3.

therefore only applicable for a vinyl chloride hazard concentration limit of 10 x TLV●, or 0.13 g/m^3. Also, data are provided up to a maximum hazard distance downwind of 100 km.

Under weather condition D, the wind speed (U) range applicable is 1 to 30 m/s. The range of instantaneous vapour emission rates (Q/T) used was 0.01 to 4100 tonnes, respectively. If the entire contents of an 80 000 L (17 600 Imp. gal.) tank car spill, the mass spilled would be 77 500 kg or approximately 78 tonnes. Therefore, under class D of Table 9, data are provided for up to 52 times this amount.

Under weather condition F, the wind speed (U) range applicable is 1 to 3 m/s. The range of instantaneous vapour emission rates ($Q/_T$) used was 0.01 to 190 tonnes, respectively. Therefore, under class F of Table 9, data are provided for up to 2.4 times a standard rail car load.

Use: Knowing the weather condition and Q_T, pick the closest value in the table and corresponding $(W/2)_{max}$, the maximum puff hazard half-width, in metres. (For an intermediate value, interpolate Q_T and $(W/2)_{max}$ values.) Also refer to the example at the bottom of Table 9.

5.3.2.3 Figure 17: Puff travel time versus travel distance. Figure 17 presents plots of puff travel time (t) versus puff travel distance (X_t) as a function of different wind speeds (U). This is simply the graphical presentation of the relationship $X_t = Ut$ for a range of typical wind speeds.

Use: Knowing the time (t) since the spill occurred and the wind speed (U), the distance (X_t) can be determined which indicates how far downwind the puff has travelled.

5.3.3 Sample Calculation. The sample calculation given below is intended to outline the steps required to estimate the downwind hazard zone which could result from a spill of liquid vinyl chloride. The user is cautioned to take note of the limitations in the calculation procedures described herein and in the Introduction Manual. The estimates provided here apply only for conditions given. It is recommended that the user employ known or observational estimates (i.e., of the spill quantity) in a particular spill situation if possible.

Problem:

During the night, at about 2:00 a.m., 20 tonnes of liquid vinyl chloride were spilled on a flat ground surface. It is now 2:05 a.m. The temperature is 20°C and the wind is from the NW at 7.5 km/h. Determine the extent of the vapour hazard zone.

Solution:

Step 1: Quantity spilled is given, Q_T = 20 tonnes

- Q_T = 20 tonnes x 0.25 (assuming 25 percent instantaneous vapour) = 5 tonnes
- $Q_T = 5 \times 10^6$ g

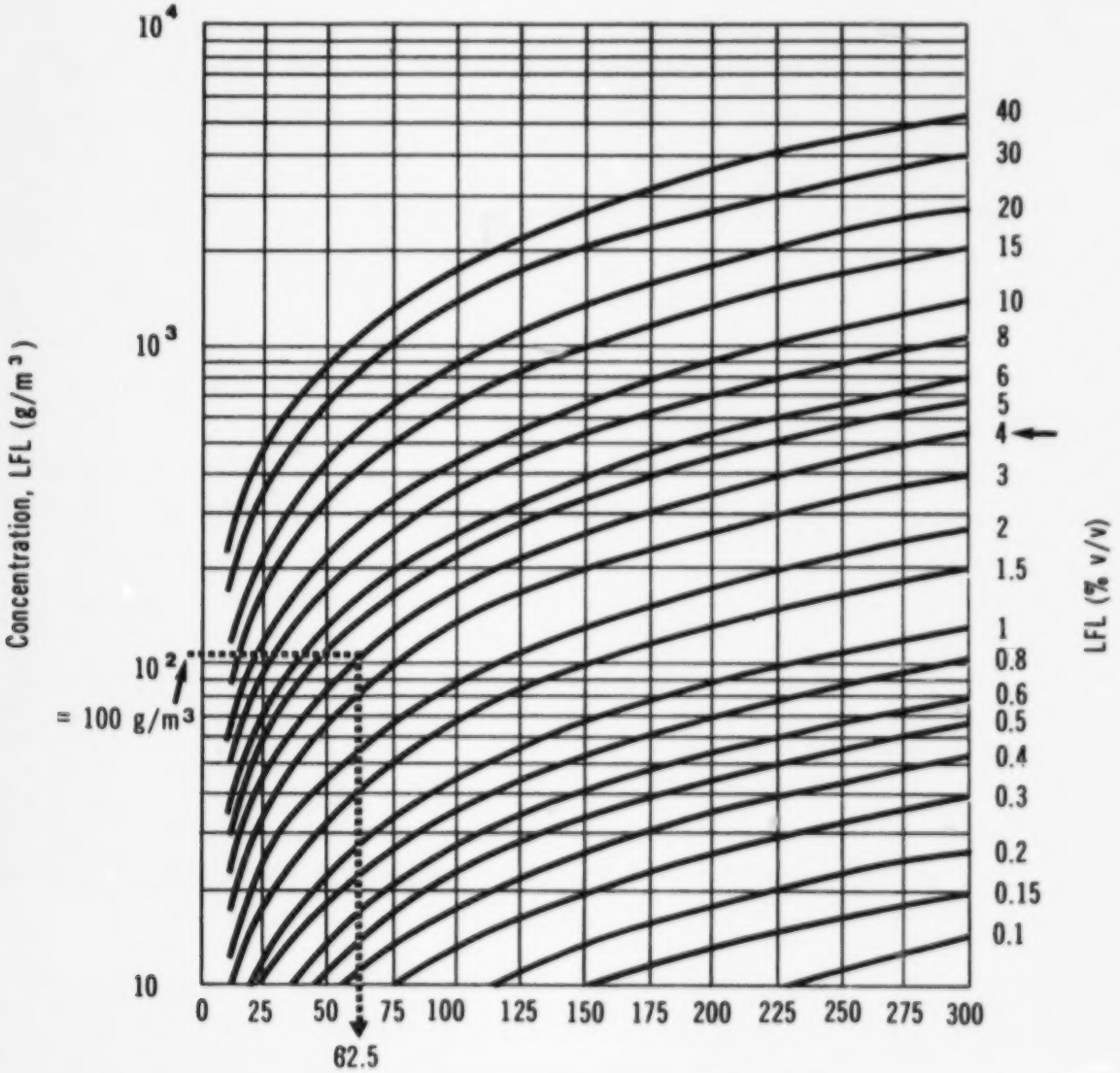
Step 2: Determine the wind speed (U) and direction (D)

- Use available weather information, preferably on-site observations

FIGURE 17

VINYL CHLORIDE

CONVERSION OF LOWER FLAMMABILITY LIMIT (LFL) UNITS (volume % to g/m³)



Example: Vinyl Chloride, MW = 62.5, LFL = 4%, then LFL in g/m³ = 100

Note: data applicable at 25°C and 760 mm Hg pressure

- Given: U = 7.5 km/h, then U = 7.5 ÷ 3.6 = 2.1 m/s
  D = NW or 315° (D = Direction from which wind is blowing)

Step 3: Determine the weather condition

- From Table 8, weather condition = F since U is less than 11 km/h and it is night

Step 4: Determine the hazard concentration limit (C)

- This is the lower of 10 times the TLV•, or the LFL, so for vinyl chloride C = 0.13 g/m^3 (TLV• = 0.013 g/m^3; LFL = 100 g/m^3)

Step 5: Compute C/Q_T

- $C/Q_T = \frac{0.13}{5 \times 10^6} = 2.6 \times 10^{-8}$ m^{-3}

Step 6: Calculate the hazard distance (X) from the instantaneous point source

- From Figure 14, with $C/Q_T = 2.6 \times 10^{-8}$ m^{-3} and weather condition F, X = 16 km

Step 7: Calculate the puff hazard half-width $(W/2)_{max}$

- Use Table 9
- With Q_T = 5 tonnes
- Then for weather condition F, $(W/2)_{max}$ = 395 m

Step 8: Determine the time since the spill

- t = 5 min x 60 = 300 s

Step 9: Calculate the distance travelled (X_t) by the vapour puff since the time of the accident

- Using Figure 17, with t = 300 s and U = 7.5 km/h, then X_t = 0.6 km (more accurately from X_t = Ut = 2.1 m/s x 300 s = 630 m = 0.63 km)

Step 10: Map the hazard zone

- This is done by drawing a rectangular area with dimensions of twice the maximum puff hazard half-width (395 m) by the maximum hazard distance downwind of the instantaneous point source (16 km) along the direction of the wind, as shown in Figure 18
- If the wind is reported to be fluctuating by 20° about 315° (or from 315° ± 10°), the hazard zone is defined as shown in Figure 19

FIGURE 18

VINYL CHLORIDE

HAZARD AREA FOR STEADY WINDS, EXAMPLE PROBLEM

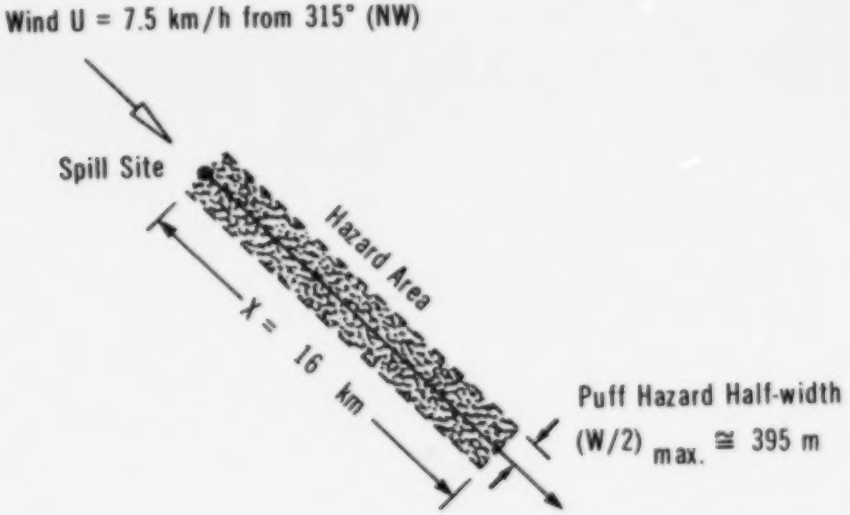
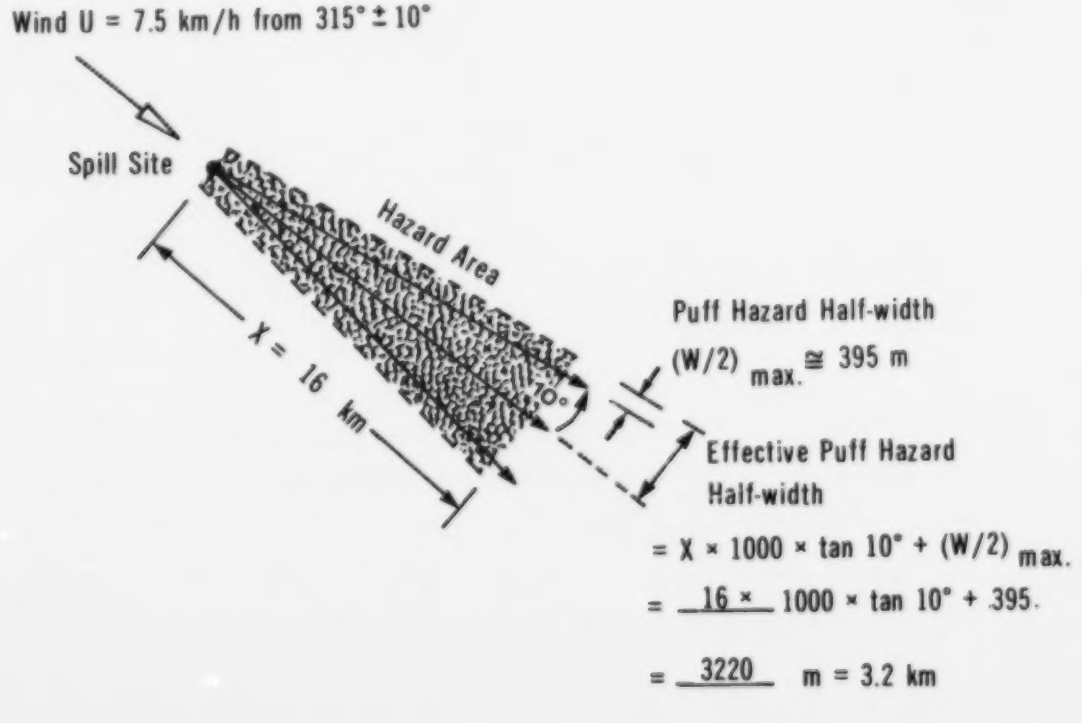


FIGURE 19

VINYL CHLORIDE

HAZARD AREA FOR UNSTEADY WINDS , EXAMPLE PROBLEM


Wind U = 7.5 km/h from 315° ± 10°
Spill Site
Hazard Area
X = 16 km
10°
Puff Hazard Half-width
(W/2) max. ≅ 395 m
Effective Puff Hazard
Half-width
= X × 1000 × tan 10° + (W/2) max.
= 16 × 1000 × tan 10° + 395.
= 3220 m = 3.2 km

- Note that the puff has only travelled 0.63 km in the 5 minutes since the spill. At a wind speed of 7.5 km/h, there remain 123 minutes before the puff reaches the maximum downwind hazard distance of 16 km

5.4 Behaviour in Water

5.4.1 Introduction. When spilled on water, vinyl chloride will vaporize and at the same time spread on the surface. Because it is only slightly soluble, a very small amount will be dissolved in the water, the rest evaporating until it is removed.

For the purpose of nomogram preparation, the extent of spread on the surface of the water has been estimated, assuming that none of the vinyl chloride is dissolved in the water. However, the loss due to vaporization has been taken into account.

The rate of spreading on water is based on the balance of forces tending to spread the liquid (gravity and surface tension) and those tending to resist spreading (inertial and viscous forces). Since cryogenic liquids such as vinyl chloride are evaporated quickly, only the initial gravity-inertia regime of spread is considered relevant (Raj 1974). The maximum size of the spill pool depends to a large extent on the rate of vaporization.

The equations representing the spreading of the spill on water are presented in the Introduction Manual. For the purposes of the nomogram presented, the water temperature has been taken at 20°C, representing a maximum for surface water bodies. This condition maximizes the spill size.

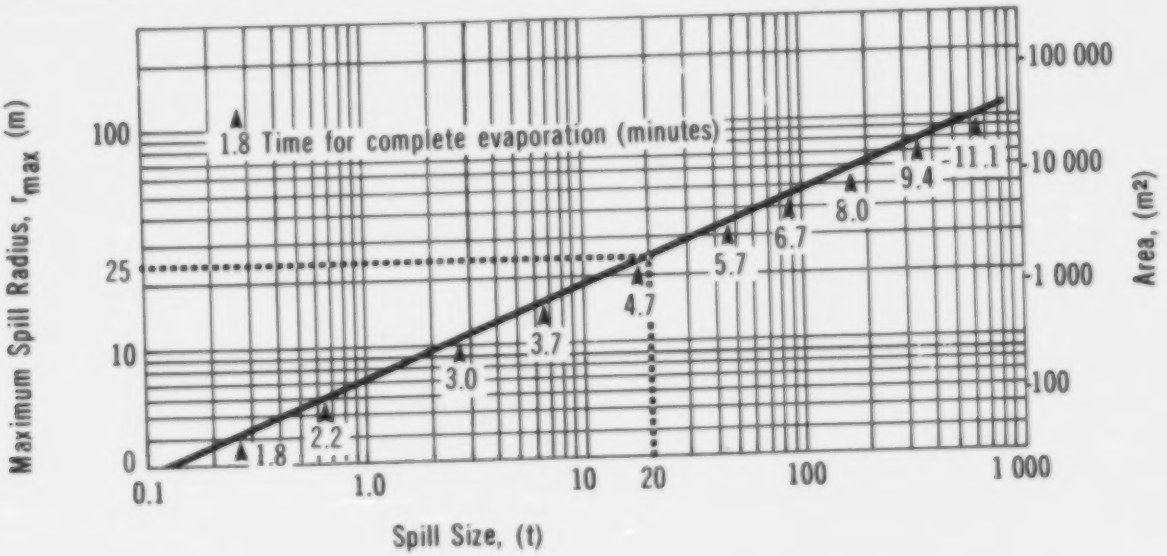
5.4.2 Nomogram for Spreading on Still Water. Figure 20 is presented to simplify the calculation of spreading on still water (without dissolution) and to estimate the time for complete evaporation for a range of spill sizes. Assuming no dissolution in water, Figure 20 provides a simple means of estimating the maximum spill radius for vinyl chloride if the spill size is known. The nomogram is based on data presented in the Hazard Assessment Handbook (CHRIS 1974) and a computer model for simultaneous spreading and evaporation of a cryogenic liquid spilled on water (Raj 1974). The bracketed figures on the nomogram provide an estimate of time for complete evaporation of the spill. Because of the short times involved, the complete time history of the spread of the spill has not been considered. Similarly, the translation distance of the spill by wind or surface current is not considered.

5.4.3 Sample Calculation. A 20 tonne spill of vinyl chloride has occurred on a large lake. What is the maximum size of the spill (assuming no dissolution) and approximate time for complete evaporation?

FIGURE 20

VINYL CHLORIDE

MAXIMUM SPILL RADIUS VS SPILL SIZE



Solution

- Use Figure 20
- With spill size = 20 tonnes, r_{max} = 25 m
- Time for complete evaporation is about 5 min

5.5 Subsurface Behaviour: Penetration into Soil

5.5.1 Mechanisms. The principles of contaminant transport in soil and their application to this work are presented in the Introduction Manual. Special considerations related to the spill of vinyl chloride onto soil and its transport downward through the soil are presented here.

Vinyl chloride is shipped as a liquefied compressed gas. It has a boiling point of -13.4°C at a pressure of 1 atmosphere. Consequently, when it is spilled onto soil, extensive evaporation will occur. While most will be lost to evaporation, the balance will infiltrate the soil. Evaporation will continue within the soil but at a reduced rate.

Vinyl chloride is only slightly soluble in water; thus, precipitation falling at the time of the spill or water used to flush the site will not provide dilution of the chemical. Traces may be carried in the aqueous phase into the soil but this is assumed to be negligible.

If the soil surface is saturated with moisture at the time of the spill, as might be the case after a rainfall, the spilled chemical will run off or pond and eventually evaporate.

For this work, the soils have been assumed to be at field capacity. This situation provides very little interstitial water to impede the contaminant's soil penetration and thus represents "worst case" analysis.

During downward movement, vinyl chloride may interact with the soil as well as evaporate. However, it is assumed that sufficient material will remain to allow movement toward the groundwater table.

Upon reaching the groundwater table, the contaminant will continue to move, now in the direction of flow within the capillary fringe. A "contaminated pancake" will be produced but will eventually dissipate through evaporation. This is shown schematically in Figure 21.

5.5.2 Equations Describing Vinyl Chloride Movement into Soil. The equations and assumptions used to describe contaminant movement downward through the unsaturated soil zone toward the groundwater table have been described in the Introduction Manual. Transport velocities have been based on Darcy's Law assuming saturated piston flow.

5.5.3 Saturated Hydraulic Conductivity of Vinyl Chloride in Soil. The saturated hydraulic conductivity (K_o), in m/s, is given by:

$$K_o = \frac{(\rho g)k}{\mu}$$

where: k = intrinsic permeability of the soil (m^2)

ρ = mass density of the fluid (kg/m^3)

μ = absolute viscosity of the fluid (Pa•s)

g = acceleration due to gravity = 9.81 m/s^2

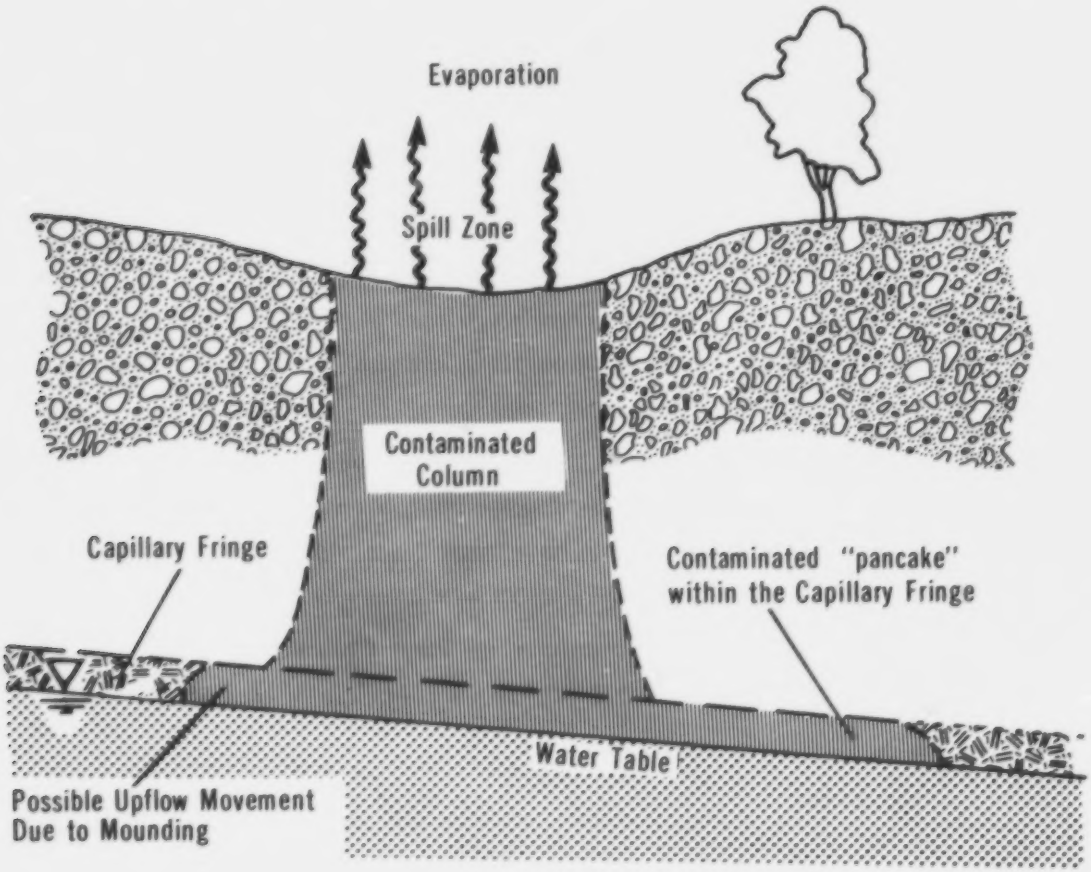
The appropriate fluid properties are shown in the chart below. Data for 4°C but not 20°C were available.

Property	4°C
Mass density (ρ), kg/m^3	939
Absolute viscosity (μ), Pa•s	0.24×10^{-3}
Saturated hydraulic conductivity (K_o), m/s	$(1.53 \times 10^7)k$

FIGURE 21

VINYL CHLORIDE

SCHEMATIC SOIL TRANSPORT



Soil: Coarse Sand

–Porosity (n) = 0.35

–Intrinsic Permeability (k) = 10^{-9} m^2

–Field Capacity (θ_{fc}) = 0.075

5.5.4 Soils. The Introduction Manual describes the three soils selected for this work. Their relevant properties are:

	Soil Type		
	Coarse Sand	Silty Sand	Clay Till
Porosity (n), m^3/m^3	0.35	0.45	0.55
Intrinsic permeability(k), m^2	10^{-9}	10^{-12}	10^{-15}
Field capacity (θ_{fc}), m^3/m^3	0.075	0.3	0.45

5.5.5 Penetration Nomograms. A nomogram for the penetration of vinyl chloride into the unsaturated zone above the groundwater table was prepared for coarse sand only. Penetration times for the denser soils, silty sand and clay till, would be several orders of magnitude greater than for coarse sand. Evaporation during this period would leave little or no contaminant for infiltration. Thus, spills on these denser soils should not result in groundwater pollution problems.

The nomogram presents penetration time (t_p) plotted against depth of penetration (B). Because of the methods and assumptions used, the penetration depth should be considered as a maximum depth in time t_p. A flowchart for use of the nomogram is presented in Figure 22. The nomogram is presented as Figure 23.

Since vinyl chloride is immiscible in water, some may remain within the soil pores as a residual during transport. This has been neglected, however, since the material will eventually evaporate.

5.5.6 Sample Calculation. A 20 tonne spill of vinyl chloride has occurred on coarse sand. The temperature is 4°C; the spill radius is approximately 8.6 m. Calculate the depth of penetration 10 minutes after the spill and check the corresponding evaporation loss.

Solution

Step 1: Define parameters

- Mass spilled = 20 000 kg (20 tonnes)
- T = 4°C

FIGURE 22

VINYL CHLORIDE

FLOWCHART FOR NOMOGRAM USE

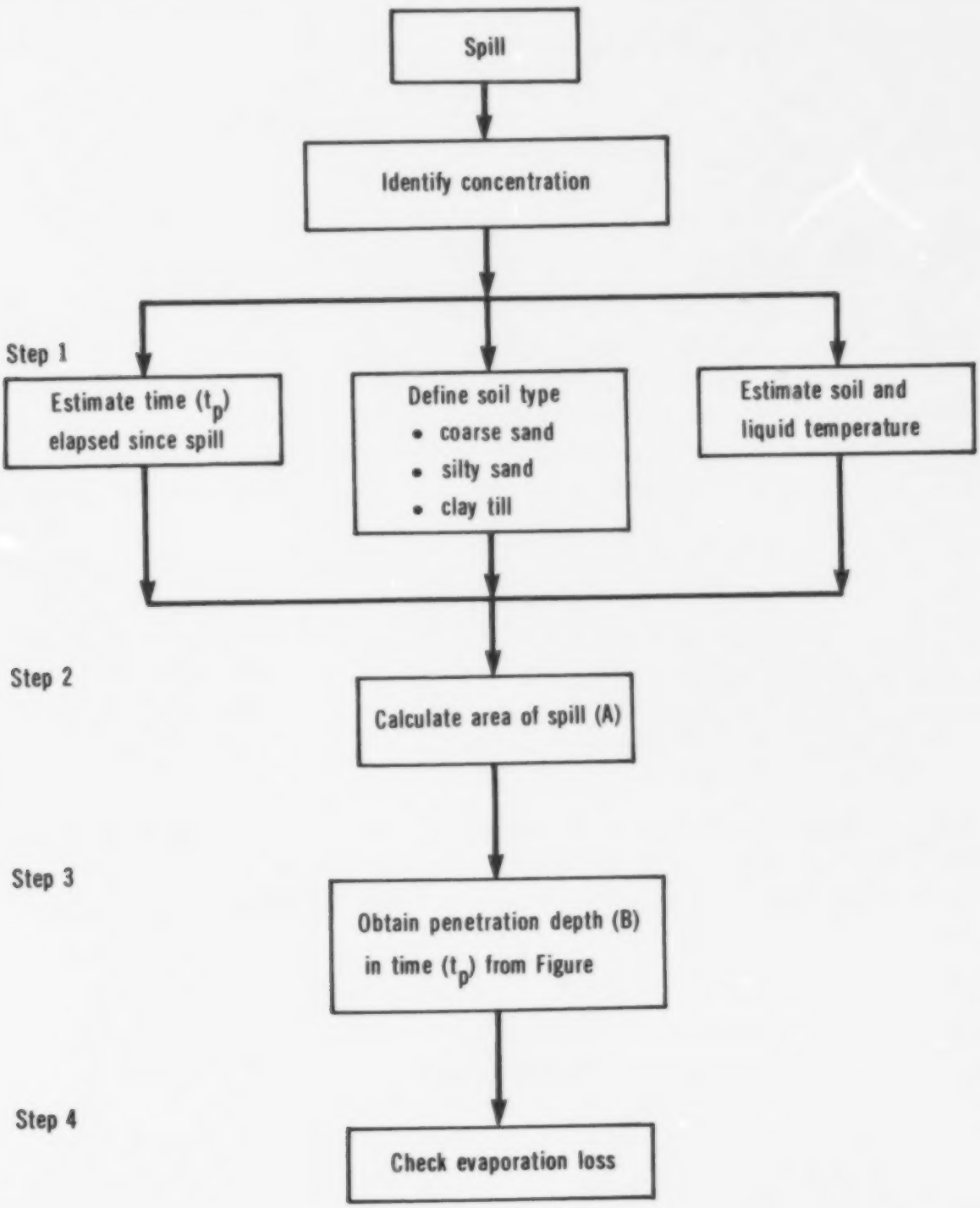
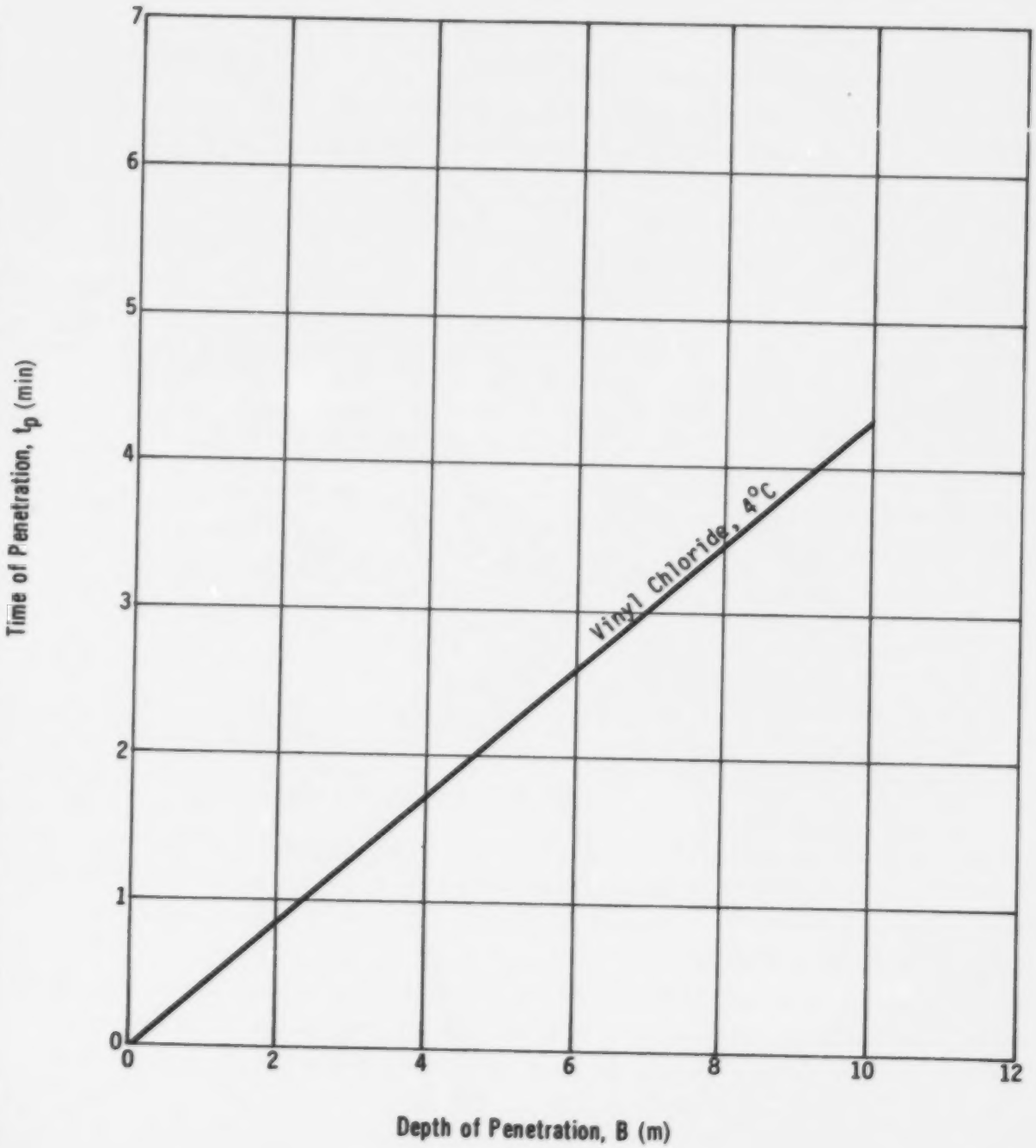


FIGURE 23

VINYL CHLORIDE

PENETRATION IN COARSE SAND



- $r = 8.6$ m
- Soil = coarse sand
- Groundwater table depth (d) = 13 m
- Time since spill (t_p) = 10 min

Step 2: Calculate the area of the spill

- $A = \pi r^2 = 232\ m^2$

Step 3: Estimate the depth of penetration (B) at time (t_p)

- For coarse sand, B = 22.5 m at t_p = 10 min
- Groundwater table has been reached in this time

6 ENVIRONMENTAL DATA

6.1 Suggested or Regulated Limits

6.1.1 Water. The U.S. Environmental Protection Agency has recommended, for maximum health protection, a concentration limit of 0 vinyl chloride in drinking water (PTP 1980). Consideration was given to setting criteria of 0.517, 0.0517 or 0.00517 mg/L for various risk levels (AWQC 1978).

6.1.2 Air. The U.S. Environmental Protection Agency proposed a stack emission limit of 10 ppm in 1975, corresponding to emissions of about 10 kg/h per average-sized plant (PTP 1980; EPA Std. 1975).

Canada has a limit for vinyl chloride content of exhaust gases of 10 ppm, or 2 kg/d, whichever is greater (Clean Air Act 1978). Ontario's limit is 560 $\mu g/m^3$ emissions, at point of impingement, with a goal of 280 $\mu g/m^3$ for ambient air (Ontario Tentative Standards 1982). A guideline for ambient air is 0.2 ppm - 1/2 hour average (APCD 1978).

6.2 Aquatic Toxicity

6.2.1 Toxicity Ratings and Aquatic Effects. Vinyl chloride has been assigned a TL_m96 of greater than 1000 ppm (RTECS 1979). Bacteria and fungi have been subjected to 900 mg/L with no toxic effect noted (EPA 1976). The bioconcentration of vinyl chloride in fish is estimated to be a factor of 1.9 (AWQC 1980).

6.3 Other Toxicity

For mammals, vinyl chloride has anesthetic properties above 500 ppm (OHM-TADS 1981). It may act as an asphyxiant at high concentrations. Toxicity to plants varies from 10 to 10 000 ppm (in air) for a 7-day exposure period (EPA Assess. 1975).

6.4 Degradation and Long-term Fate

In water, vinyl chloride does not appear to be sorbed, degraded or affected by microorganisms, as verified by experiments with 5 mixed bacterial cultures, 3 mixed fungal populations and 2 bacterial cultures (EPA Aqua 1976). The chemical degradation in water also does not appear to be significant. Vinyl chloride is rapidly lost to the atmosphere. Effluent water from a vinyl chloride plant may contain as high as 20 ppm but more typically 2-3 ppm (EPA 1974). The rate of exchange of gaseous vinyl chloride between water and air is about twice that of oxygen (EPA Aqua 1976). On this basis, the

half-life of 1 ppm VCM in water at a 1 m depth is estimated to be 26 min (Verschueren 1984).

In air, vinyl chloride photodegrades to hydrogen chloride or formyl chloride, which in turn reacts rapidly to produce carbon monoxide and hydrogen chloride. The half-life in air is estimated to be 2 days (CIC 1977).

7 HUMAN HEALTH

Vinyl chloride is a colourless flammable gas at room temperature and pressure, with a pleasant, sweet odour at high concentrations. Human exposure to this synthetic compound is generally by inhalation and less frequently by skin absorption. Until very recently, its documented health effects were confined to Raynaud's syndrome-type symptoms (a syndrome characterized by deadening of sensations at the fingertips, whitening of fingers, and pain and sores on the hands), skin changes, bone lesions, acroosteolysis (deprivation or removal of calcium from bones in hands or feet), central nervous system depression, and disorders of the circulatory system (SOEHS 1975; EPA 1975; ICF 1974).

In 1971, a link was drawn between the inhalation of vinyl chloride monomer and malignant changes in rats. Later animal studies have further confirmed first reported cases. Subsequently, hepatic angiosarcoma (a rare form of liver cancer) cases among occupationally exposed workers were reported (SCC 1981; NTIS 1981).

In 1976, there were 48 known cases of vinyl chloride-related hepatic angiosarcomas in the world, 47 of which involved the handling of large quantities of liquefied vinyl chloride under pressure (SCC 1981). After detailed research and study, vinyl chloride is generally considered to be a confirmed human carcinogen (Doc. TLV 1981; USDHEW 1981; Doniger 1978; Senate 1974); as a result, its use has been restricted under environmental, drug, public health and regulatory laws.

Due to the tremendous usage of the chemical, its deleterious effects have been widely studied and documented. A number of agencies have reviewed vinyl chloride toxicology (VCT 1980; SCC 1976, 1981). Several reports have dealt with its carcinogenic, mutagenic and teratogenic effects. The compound is listed by the U.S. Environmental Protection Agency under the TSCA Inventory. Due to the large volume and repetitive conclusions of these tests, only the most recent or more significant of these have been documented.

The toxicological data summarized here have been extracted from reliable standard reference sources. It should be noted that some of the data are for chronic (long-term), low-level exposures and may not be directly applicable to spill situations.

7.1 Recommended Exposure Limits

The exposure standards for vinyl chloride are based upon its carcinogenic properties. Canadian provincial guidelines generally are similar to those of the USA-ACGIH unless indicated otherwise.

Guideline (Time)	Origin	Recommended Level	Reference
Time-weighted Averages (TWA)			
TLV● (8 h)	USA-ACGIH	5 ppm (10 mg/m^3)	TLV 1983
PEL (8 h)	USA-OSHA	1 ppm	NIOSH/OSHA 1981
Action Level	USA-OSHA	0.5 ppm	GE 1978
Recommended Exposure Level	USA-NIOSH	1 ppm	NIOSH Standard 1974
Time Weighted Average Exposure	Ontario	2 ppm (5.2 mg/m^3)	Ont. Reg. 1982
Permissible Concentration (8 h)	B.C.	1 ppm, carcinogen	B.C. 1980
Concentration moyenne (8 h)	Québec	1 ppm, cancérigène	Québec 1979
Carcinogenic Substance (duration unspecified)	Saskatchewan	None given, carcinogenic substance	Saskatchewan 1981
Short-term Exposure Limits (STEL)			
Ceiling (15 min sample)	USA-OSHA	5 ppm	NIOSH/OSHA 1981
Ceiling (15 min sample)	USA-NIOSH	Minimum detectable - 1 ppm	NIOSH/OSHA 1981
Concentration maximale (15 min)	Québec	1 ppm, cancérigène	Québec 1979
Maximum	Ontario	10 ppm (26 mg/m^3)	Ont. Reg. 1982
Other Human Toxicities			
IDLH		No data	
TC_{LO} (intermittent)		500 ppm	RTECS 1979

Inhalation Toxicity Index

The Inhalation Toxicity Index (ITI) is a measure of the potential of a substance to cause injury by inhalation. It is calculated as follows:

ITI = 1315.12 (Vapour pressure, in mm Hg/TLV●, in ppm)

At 20°C, ITI = 1315.12 (2524 mm Hg/5 ppm)

= 6.6×10^5

7.2 Irritation Data

7.2.1 Skin Contact.

Exposure Level (and Duration)	Effects	Reference
SPECIES: Human		
Unspecified	Sclerotic changes of the skin and various lesions.	TDB (on-line) 1981
Unspecified	Allergic dermatitis.	TDB (on-line) 1981
Unspecified	Degenerative skin changes which histologically showed destruction of the elastic network of the connective tissue (hands, forearm, face).	SOEHS 1975

7.2.2 Eye Contact.

Exposure Level (and Duration)	Effects	Reference
SPECIES: Human		
Unspecified (liquid)	Inflammation of conjunctivas and lesions in the cornea due to inflammation.	Lefèvre 1980
Unspecified (liquid)	Contact of eyes with escaping compressed vinyl chloride can produce frostbite.	Doc. TLV 1981

7.3 Threshold Perception Properties

7.3.1 Odour.

Characteristics: Mild, sweet, pleasant (Verschueren 1984)

Odour Index: 100 (20°C) (Verschueren 1984)

Parameter	Media	Concentration	Reference
Threshold Odour Concentration	In air	4000 to 25 000 ppm	Verschueren 1984
Detection Threshold	In air	1200 to 2000 ppm	AWQC 1978

7.3.2 Taste. No data.

7.4 Toxicity Studies

7.4.1 Inhalation.

Exposure Level (and Duration)	Effects	Reference
Acute Exposures		
SPECIES: Human		
25 000 ppm (3 min)	Dizziness and disorientation.	TDB (on-line) 1981
8000 to 12 000 ppm (5 min)	Intoxication signs are manifested.	ICF 1974
10 000 ppm	Noticeable anesthetic effects.	Patty 1981
4000 ppm (5 min or more)	Dizziness and confusion. Higher concentrations may lead to unconsciousness and death.	SCC 1981
1000 ppm	Slight anesthesia, drowsiness, slight visual disturbances, faltering gait, numbness and tingling of extremities.	TDB (on-line) 1981
500 ppm	TC_{LO}	DPIMR 1981
Unspecified	After "massive" and apparently repeated exposures: euphoria followed by a state of inebriation similar to that of alcohol intoxication, epigastric pain and anorexia.	TDB (on-line) 1981
Unspecified	Two deaths reported from accidental acute VC poisoning. Cyanosis, local burns, congestion of lungs and kidneys, and failure of the blood to clot were noted.	SCC 1981

Exposure Level (and Duration)	Effects	Reference
SPECIES: Dog		
170 000 ppm (1 min)	Narcosis	EPA Assess. 1975
100 000 ppm (4 h)	Cardia arrhythmia	EPA Assess. 1975
SPECIES: Mice		
86 000 to 123 000 ppm (1 min)	Narcosis	EPA Assess. 1975
SPECIES: Guinea Pig		
200 000 ppm (18 min)	Death	INRS 1975
20 000 ppm (30 min)	TC_{LO}	DPIMR 1981
5000 ppm (30-60 min)	Pulmonary edema, hyperemia of kidneys and lungs.	INRS 1975
SPECIES: Rat		
6000 ppm (4 h)	TC_{LO}	DPIMR 1981
Chronic Exposures		
SPECIES: Human		
Unspecified	In 168 workers, the incidence of Raynaud's syndrome was reported as 6 percent and the incidence of liver enlargement as 30 percent.	TDB (on-line) 1981
Unspecified	Several studies of workers exposed to VCM showed various degrees of liver damage (usually enlarged liver) and enlarged spleens.	EPA Assess. 1975
Unspecified	Clinical examination of exposed workers in Dundee Research Project - deficient circulation in the extremities (Raynaud's Phenomenon); osteolysis of terminal phalanges of the fingers and to a lesser extent of the toes; degenerative skin changes with destruction of the elastic network of the connective tissue;	SOEHS 1975

Exposure Level (and Duration)	Effects	Reference
	paresthesia of the fingers with thickening of the end segments; general symptoms of fatigue, breathlessness on exertion, dizziness, increased sweating, and pains in the upper epigastric region.	
Unspecified	Three thousand workers employed in the PVC manufacturing industry were examined. Acroosteolysis with or without Raynaud's syndrome was found in 31 of these.	SOEHS 1975
Unspecified (mean 7 yr, 2 yr and 18 yr)	Thirteen autoclave workers, mean age 39, showed first symptoms from 1-1/2 to 3-1/2 years after exposure began. Found Raynaud's syndrome, clubbing and shortening of the fingers, skin changes resembling scleroderma, with disorders of the circulatory system being the most common symptom. Laboratory tests showed reduced liver function in 11 of the workers.	SOEHS 1975
Unspecified	Thirteen PVC workers showed similar symptoms to those listed above. Two of the men who had been removed from exposure, one for 6 months and one for 1-1/2 year, subsequently developed signs and symptoms of VCM disease in hands and feet.	SOEHS 1975
Unspecified	After repeated chronic exposures, the main neurological symptoms were headaches, irritability, dizziness, sleep disorders, diaphoresis, memory loss, general asthenia and paresthesia.	SCC 1981

7.4.2 Ingestion.

Exposure Level (and Duration)	Effects	Reference
SPECIES: Rat		
500 mg/kg	LD_{50}	RTECS 1979

7.4.3 Carcinogenicity.

Exposure Level (and Duration)	Effects	Reference
SPECIES: Human		
500 ppm (4 yr, intermittent)	TC_{LO}, carcinogen.	RTECS 1979
200 ppm (15 yr, intermittent)	Inhalation - equivocal tumorigenic agent.	RTECS 1979
Unspecified	Report of four deaths at B.F. Goodrich Chemical Company caused by the rare angiosarcoma of the liver. On investigation, NIOSH concluded vinyl chloride was a probable occupational carcinogen.	NIOSH Standard 1974
Unspecified	As of March 1976, there were 48 known cases of vinyl chloride related liver angiosarcomas, 45 of which had resulted in death. All 9 of the Canadian cases worked in one plant in Shawinigan, Québec, and 9 of the U.S. cases worked in one plant. These deaths had occurred over a period of 14 years, with the number per year showing an increase with time.	SCC 1981
Unspecified	A study of former Monsanto Company chemical plant employees has shown an increased incidence of cancer among workers	COHSN 1982

Exposure Level (and Duration)	Effects	Reference
	exposed to vinyl chloride; 34 of 110 deaths were from cancers: lung, mouth, digestive system and lymph glands. One death was due to liver cancer. Only worksites where there had been exposure to vinyl chloride and polyvinyl chloride were examined.	
Unspecified	In addition to liver angiosarcomas, lung cancer has been found in some epidemiological studies.	Lilis 1981; Apfeldorf 1981
Unspecified	A study of VCM and PVC processing works revealed that in the VCM cohort there were significantly elevated mortality rates due to malignancy of the lymphatic gland and hematopoietic tissues and the gastrointestinal tract, the latter primarily due to tumours of the liver.	Weber 1981
1-10 ppm (long-term)	The long-term effects such as angiosarcoma, liver damage, Raynaud's syndrome may be due to levels as low as 1-10 ppm; onset of angiosarcoma is estimated to be 13-20 years; however, a few rare cases of shorter times (3-6 yr) were found.	EPA Assess. 1975
1 ppm (5 h/day, 5 d/wk, 35 yr)	A study of epidemiological results and various statistical models places the risk of liver angiosarcoma at 1.5×10^{-8} (5 out of a million) at this dosage.	Gehring 1979
SPECIES: Rat		
50 000 ppm-h	Carcinogenic dose calculated from various concentrations and times including single doses.	Hehir 1981

Exposure Level (and Duration)	Effects	Reference
6000 ppm (4 h/d 12 to 18 of pregnancy)	TC_{LO}, carcinogenic effect (inhalation).	RTECS 1979
600 ppm (8 h/d, 5 d/wk)	Angioscarcoma in 23 percent of animals; this was increased to 50 percent by administration of ethanol in water (5 percent by volume). It was concluded that ethanol is a co-carcinogen in relation to vinyl chloride.	Radike 1981
250 ppm (39 wk)	Toxic dose, carcinogenic effect (inhalation).	RTECS 1979
250 ppm (35 wk)	Toxic concentration, carcinogenic effect (inhalation).	RTECS 1979
50 ppm (30 wk)	TC_{LO}, carcinogenic effect (inhalation).	RTECS 1979
34 g/kg (3 yr)	Toxic concentration, carcinogenic effect (oral).	RTECS 1979
11 g/kg (3 yr)	TD_{LO}, carcinogenic effect (oral).	RTECS 1979
250, 500, 2500, 6000, 10 000 ppm (127 wk)	Induction of angiosarcoma in the liver and other organs, and other cancers. The percentage of animals having liver angiosarcomas varied but was around 10 percent; 50 ppm exposure resulted in no angiosarcomas.	Maltoni 1974. IN NIOSH Standard 1974; ICF 1974
SPECIES: Hamster		
500 ppm (4 h/d for 30 wk)	TC_{LO}, carcinogenic effects (inhalation).	RTECS 1979
SPECIES: Mouse		
5000 ppm-h	Carcinogenic dose for mice determined by a variety of exposure periods and concentrations.	Hehir 1981
2500 ppm (5 h/d for 26 wk, intermittently)	Toxic dose, neoplastic effects (inhalation).	RTECS 1979

Exposure Level (and Duration)	Effects	Reference
250 ppm (35 wk, intermittently)	Toxic concentration, carcinogenic effects (inhalation).	RTECS 1979
50 ppm (30 wk, intermittently)	TC_{LO}, carcinogenic effects (inhalation).	RTECS 1979
50 ppm (6 h/d for 12 wk, intermittently)	Toxic dose (inhalation).	RTECS 1979
SPECIES: Animal, unspecified		
25 ppm (4 h/d for 1 yr)	5 liver angiosarcomas, 4 zymbal gland carcinomas and 1 nephroblastoma in 120 test animals.	Patty 1981
SPECIES: Rats, Mice, Hamsters		
0-30 000 ppm (various exposures from single to 52 wk) (inhalation) 0.03 to 50 mg/kg (single dose to 5/wk for 52 wk) (ingestion or injection)	A major study involving 7000 animals of various species, strains, and sexes was conducted. The results indicate that vinyl chloride is a multi-potential carcinogen affecting a variety of organs and tissues. Liver angiosarcoma was detected in all species; many types of tumours were found. Vinyl chloride shows carcinogenic effects whether it was administered by inhalation or ingestion and shows a clear dose-response relationship. Newborn animals are the most sensitive. Vinyl chloride shows carcinogenic effects even down to 50 ppm.	Maltoni 1981
10 ppm (4 h/d for 1 yr)	1 liver angiosarcoma, 2 extrahepatic angiosarcomas and 2 zymbal gland sarcomas in 120 test animals.	Patty 1981
1 mg/kg	3 liver angiosarcomas, 1 extrahepatic angiosarcoma and 1 hepatoma in 150 animals.	Patty 1981

7.4.4 Teratogenicity and Mutagenicity.

Exposure Level (and Duration)	Effects	Reference
SPECIES: Human		
Unspecified	Increased frequency of chromosomal aberrations in lymphocytes of exposed workers.	NIOSH/OSHA Bulletin 1978
Unspecified	Increased fetal wastage among wives of male workers who have had occupational exposure to vinyl chloride.	NIOSH/OSHA Bulletin 1978; Hatch 1981
Unspecified	An epidemiological study was made of an area where the general population was exposed to VCM. The population was shown to have an excess of birth defects compared to other communities; the fluctuation in defects corresponded with VCM fluctuations in the environment.	Laval 1981
Unspecified	An epidemiological study of workers in a plastic/rubber plant revealed a greater percentage of chromosomal breakage compared to workers in other industries; however, the breakage did not correlate to VCM exposure and thus another agent(s) is suspected.	Heath 1977
SPECIES: Rat		
1500 ppm (during the first, second or third trimester of pregnancy)	Increased fetal mortality and other fetotoxic effects when administered during the first trimester; no embryotoxicity was noted when vinyl chloride was administered during the second or third trimester.	Patty 1981
SPECIES: Chinese Hamster		
2500 or 5000 ppm (4 h/d for 5 d)	Chromosomal changes in bone marrow cells.	Patty 1981

Exposure Level (and Duration)	Effects	Reference
SPECIES: Hamster		
600 mg/kg	Cytogenic analysis assaying for chromosomal aberrations following administration of vinyl chloride (in vivo). No results reported.	RTECS 1979
20 pph (5 h)	Hamster lung cells were tested using microsomal mutagenic assay. No results reported.	RTECS 1979
SPECIES: Mouse		
3000, 10 000 or 30 000 ppm for 5 d	No dominant lethal effects.	Patty 1981
SPECIES: *Drosophila melanogaster*		
1 pph	Sex chromosome loss and non-disjunction tests have been performed (in vivo). Route of administration was by inhalation.	RTECS 1979
SPECIES: *Salmonella typhimurium*		
11 percent (in air)	Positive Ames test - concluded that vinyl chloride induced point mutagens but only after metabolic conversion.	Senate 1974
2 to 20 percent (in air)	Positive Ames test results by several investigators.	Fabricant 1981

7.5 Symptoms of Exposure

General symptoms of exposure found in most information sources have not been specifically referenced. Only those of a more specified or unusual nature have their sources indicated.

7.5.1 Inhalation.

1. Irritation of nose and throat.
2. Headache.

3. Overexcitement (TDB (on-line) 1981).
4. Anesthetic effects (Patty 1981).
5. Narcosis.
6. Numbness and tingling of extremities (TDB (on-line) 1981).
7. Visual disturbances (TDB (on-line) 1981).
8. Dizziness and disorientation.
9. Inebriation.
10. Faltering gait.
11. Euphoria.
12. Epigastric pain (TDB (on-line) 1981).
13. Anorexia.
14. State of shock (Lefèvre 1980).
15. Loss of consciousness.
16. Coma.
17. Death as a result of cardiac or respiratory failure (Lefèvre 1980).

7.5.2 Ingestion.

Ingestion is unlikely; however, if ingested, vinyl chloride would be toxic and cause tissue damage (AAR 1981).

7.5.3 Skin Contact.

1. Dry skin.
2. Allergic dermatitis (TDB (on-line) 1981).
3. Frostbite.
4. Irritation and burns from absorption of phenol stabilizer (GE 1978).
5. Various lesions.

7.5.4 Eye Contact.

1. Irritation.
2. Inflammation of conjunctiva.
3. Corneal lesions due to inflammation (Lefèvre 1980).

7.6 Human Toxicity to Decay or Combustion Products

Polyvinyl chloride breaks down into hydrogen chloride and carbon dioxide when subjected to excessive heat or pressure. Extensive studies have shown that phosgene has not been detected under any practical circumstances (SCC 1976), although some sources

report this product (GE 1979). Similar decomposition products might be expected when vinyl chloride burns.

7.6.1 Carbon Dioxide and Hydrogen Chloride. Carbon dioxide is a colourless, odourless gas which in elevated concentrations may act to produce mild narcotic effects, respiratory stimulation and asphyxiation. Its TLV® is 5000 ppm (8 h - TWA) and 15 000 ppm (STEL) (TLV 1983).

Hydrogen chloride may be present as a gas or a liquid. In contact with human skin it causes irritation, inflammation, burns, blistering dermatitis and profound tissue damage, depending upon concentration and length of contact. In contact with eyes it can cause stinging, burning, opaqueness of the cornea and corneal necrosis. Inhalation causes coughing, choking, ulceration of the mucosa, bronchitis, pneumonia and, in cases of exposures to extremely high concentrations, pulmonary edema and death. The TLV® is 5 ppm (8 h - TWA) (TLV 1983).

8 CHEMICAL COMPATIBILITY

8.1 Compatibility of Vinyl Chloride with Other Chemicals and Chemical Groups

SPECIFIC CHEMICAL OR CHEMICAL GROUP	HEAT GENERATION	FIRE	EXPLOSION	FORMATION OF FLAMMABLE GASES	VIOLENT POLYMERIZATION	DECOMPOSITION	FORMATION OF TOXIC FUMES	FORMATION OF SUBSTANCES OF GREATER TOXICITY	PRESSURIZATION IN CLOSED VESSELS	SOLUBILIZATION	VIOLENT REACTION	NON-HAZARDOUS REACTION	SPECIFICS	REFERENCE
GENERAL														
Air			•										Forms an unstable polyperoxide which can initiate an explosion	Bretherick 1979
Fire	•	•				•							Large vinyl chloride fires are practically inextinguishable; vapour may flash back	Sax 1979; NFPA 1978
Heat				•									Polymerization may take place, with possible container rupture	NFPA 1978
CHEMICAL GROUPS														
Catalytic Metals			•										Polymerization can be initiated by catalytic metals such as copper, aluminum and their alloys	CCPA 1983

8.1 Compatibility of Vinyl Chloride with Other Chemicals and Chemical Groups (Cont'd)

SPECIFIC CHEMICAL OR CHEMICAL GROUP	HEAT GENERATION	FIRE	EXPLOSION	FORMATION OF FLAMMABLE GASES	VIOLENT POLYMERIZATION	DECOMPOSITION	FORMATION OF TOXIC FUMES	FORMATION OF SUBSTANCES OF GREATER TOXICITY	PRESSURIZATION IN CLOSED VESSELS	SOLUBILIZATION	VIOLENT REACTION	NON-HAZARDOUS REACTION	SPECIFICS	REFERENCE
CHEMICAL GROUPS														
Nitrides	•			•										EPA 600/2-80-076
Organic Peroxide	•			•										EPA 600/2-80-076
Oxidizing Agents	•	•				•								EPA 600/2-80-076

9 COUNTERMEASURES

9.1 Recommended Handling Procedures

The following procedures have been derived from a literature review. To avoid any deviation from the intended meaning, the wording of the original source has been presented essentially unchanged - in so doing, it is recognized that there may be discrepancies between different sources of information. It is recognized that countermeasures are dependent on the situation, and thus what may appear to be conflicting information may in fact be correct for different situations. The following procedures should not be considered as Environment Canada's recommendations.

9.1.1 Fire Concerns. Vinyl chloride is an extremely flammable gas. It readily forms explosive mixtures in air (GE 1978). Its vapours may travel along surfaces to ignition sources and flash back (NFPA 1978). It can undergo hazardous exothermic polymerization if heated or if reaction is catalyzed (GE 1978).

9.1.2 Fire Extinguishing Agents. Stop leak before attempting to extinguish fire. Use water spray at a safe distance to cool containers involved in a fire to prevent rupture or explosion (ERG 1980).

Small fires: Dry chemical, or CO_2.

Large fires: Water spray, fog or foam.

Move containers from fire area if this can be done without risk. Stay away from tank ends. For massive fires, use unmanned hose holder or monitor nozzles (ERG 1980).

9.1.3 Evacuation. In the event of an explosion, the minimum safe distance from flying fragments is 600 m in all directions. Keep internal combustion engines and other sources of ignition at least 20 m from probable ignition area (EAG 1978).

9.1.4 Spill Actions.

9.1.4.1 General. Stop or reduce discharge of material if this can be done without risk. Eliminate all sources of ignition. Avoid skin contact and inhalation (Dow ERIS 1981). Controllable leaks of vinyl choride in containers can be plugged by driving wooden plugs in small holes and/or applying a neoprene patch for larger holes. The patch should be bonded or chained to the containers to make it secure (MCA 1972). Special kits for VCM tank car leak plugging are available (VCM 1982).

For larger, uncontrollable leaks, control spread of vapours by water spray. Make provisions to minimize the mixing of air with VCM vapour in confined spaces and the burning containers. The use of water, N_2 or any inert gas is recommended to prevent explosions (MCA 1972).

Application of a fluorocarbon water foam is recommended to diminish vapour and fire hazard (EPA 670/2-75-042). Tests of various foams revealed that most low expansion foams will reduce the vapour emission from a pool by a factor of about 2 (MSA 1982).

9.1.4.2 Spills on land. If liquid vinyl chloride is spilled on land, contain if possible by forming mechanical and/or chemical barriers to prevent spreading (EPA 670/2-75-042). If the ambient temperature is low (e.g., VCM does not evaporate rapidly), vinyl chloride can be pumped into appropriate containers for return to the manufacturer. This process must be conducted with extreme care, with correct equipment and trained individuals. Otherwise, the only safe countermeasure is to let the VCM evaporate.

9.1.4.3 Spills on water. Control, if possible, by using natural barriers or booms to limit spreading. Remove trapped material with suction hoses or pumps, using extreme caution (EPA 670/2-75-042). Otherwise, the only safe method is to let the material evaporate.

9.1.5 Cleanup and Treatment.

9.1.5.1 Spills on water. When vinyl chloride is spilled on water, activated carbon can be applied at 10 percent the spill amount over the region occupied by 10 mg/L or greater concentrations. Mechanical dredges or lifts can then be used to remove the carbon (EPA 670/2-75-042). Aeration of contaminated water will also substantially remove vinyl chloride.

9.1.5.2 General. The following treatment processes have shown possible applicability for spill countermeasures:

Process	Percent Removal (TSA 1980)	Process	Maximum Percent Removal (EPA 600/8-80-042E)
Biological	100	Granular Activated Carbon Adsorption	52

9.1.6 Disposal. Waste vinyl chloride must never be discharged directly into sewers or surface waters. Vinyl chloride monomer can be burned in a high-temperature incinerator with a scrubber attached to remove any hydrochloric acid formed (GE 1978).

9.1.7 Protective Measures. For entry into a situation where the spilled material and its characteristics are unknown, self-contained breathing apparatus and a totally encapsulated chemical suit should be worn.

If the spilled material is known to be vinyl chloride:

- Impervious clothing and self-contained breathing apparatus should be worn (Dow ERIS 1981; GE 1978).
- The following clothing materials shows breakthrough times of approximately 1 hour: butyl rubber, polyurethane, styrene-butadiene rubber, and Viton (Little 1983).
- Any clothing which becomes contaminated with VCM should be removed immediately and thoroughly washed and dried before reuse (MCA 1972).
- Eye wash stations and chemical safety showers should be readily available in areas of use and spill situations (GE 1978).

The following is a list of the minimum respiratory protection recommended for personnel working in areas where vinyl chloride monomer is present (GE 1978). It should be noted that conventional activated charcoal respirators have a very low absorption capacity for vinyl chloride. In tests run at 50 ppm and 50 percent relative humidity, the breakthrough time is 40 minutes. At 100 ppm and the same relative humidity, the breakthrough time is 160 minutes. In high relative humidities, this time is lower (NIOSH 1974).

Condition	Respiratory Protection
Vapour Concentration	
Up to 10 ppm	Organic cartridge-type respirator.
Up to 25 ppm	Canister-type gas mask, full facepiece.
Above 25 ppm	Air supplied or self-contained type respirators.
Fire fighting	Self-contained breathing equipment.

9.1.8 Storage Precautions. Store in a cool, well-ventilated place; an outside or detached, noncombustible location is preferred. Keep away from oxidizing agents and sources of heat or ignition. Protect cylinders against physical damage (GE 1978).

9.2 Specialized Countermeasures Equipment, Materials or Systems

The following items are taken from a previous study (Dillon 1982) and should not be considered to be the only suitable specialized countermeasures equipment, materials or systems available. More details on the specifications, performance and availability of these items can be found in the referenced study.

Leak Plugging	Emergency Safety Kit for VCM Tank Cars
Chemical/Physical Modification	Ultrox (UV-Ozone) Process

10 PREVIOUS SPILL EXPERIENCE

10.1 General

This section contains information on previous spill experience which will be useful to readers in understanding spill response and countermeasures. Only those which meet the criteria are included, and thus, the number of experiences is not an indication of the problems or frequency of spillage. As technology in spill control advances, this section will be updated in future manual revisions to include the most useful information.

10.2 Train Derailment (MacGregor 1980)

A train derailment occurred in the early hours of the morning, in winter conditions, resulting in leaks in two tank cars carrying vinyl chloride. The leaks were found to be from a safety valve on one car and a hole, approximately 5 x 7 cm, in the other. The latter leak was not discovered until 4 days after the derailment.

The leak rate of vinyl chloride from the valve appeared to be low due to the ambient temperature being below the boiling point of vinyl chloride (-13.4°C). Although the vinyl chloride concentration at snow level, 1 m from one of the leaking cars, was measured at over 200 ppm, levels at the normal human breathing zone were generally very low. Unexpectedly, some of the liquid vinyl chloride released penetrated the snow cover and became trapped between the earth and snow. This was indicated by anomalous crystalline patches observed in the snow. The remainder evaporated at varying rates depending on the temperature over the spill period. Little could be done to contain or recover the vinyl chloride under these circumstances.

On the third day of the spill, the leaking safety valve was capped and wreck clearing commenced. On the fourth day, the puncture in the second tank car was discovered, indicated by "a shimmering effect, like a gas main shimmering or a hot road shimmering in the summer time". An area of 6 x 9 m was roped off for a patching operation. After first cutting away the outer shell with hand shears to prevent explosion, a preliminary patch was made up using a metal portion of a shovel and a Teflon ironing board cover as a gasket. A permanent patch was later installed by driving a wooden plug into the puncture hole and covering it with Velodur "plastic metal" which was cured by warming overnight with an antifreeze-filled hot water bottle. The next morning, this plugging device was backed up with a 1.3 cm thick steel plate, curved to the contour of the inner shell of the car and pressed onto the shell by a bolt and metal lever. The vinyl chloride was then transferred from the damaged cars to new tank cars.

An estimated 70 600 L of vinyl chloride monomer spilled from this mishap. Air monitoring was carried out both on and off site during cleanup. In general, breathing zone readings on-site were "nil" except in the immediate vicinity of the damaged cars, where levels occasionally exceeded 5 ppm (TLV•), restricting workers' access. No traces of vinyl chloride were detected in off-site air samples. In addition to air monitoring, on-site and off-site sampling programs for soil, snowmelt water, drinking water and groundwater were carried out after the cleanup. No traces of vinyl chloride were found in the drinking water, although residual traces were detected in soil, snow and groundwater. Three months after the spill, the highest vinyl chloride concentration found at groundwater level (taken from the centre of the spill site) had declined to 0.05 mg/L.

11 ANALYTICAL METHODS

The general approach adopted for each of the Priority Chemicals was as follows.

Methods have been documented here for the analysis of samples from air, water and soil in a normally equipped chemical laboratory remote from the spill site. Customary sources of standard or recommended analytical methods were consulted, and outlines are presented for each chemical. These sources included publications of the U.S. National Institute for Occupational Safety and Health (NIOSH), the U.S. Environmental Protection Agency (EPA), the American Water Works Association (AWWA), the American Society for Testing and Materials (ASTM), and the American National Standards Institute (ANSI).

If the standard or recommended methods were judged to be reliable and specific enough for the analysis of environmental and materials samples from spill sites and if they do not require highly specialized laboratory equipment, no additional methods were sought.

If especially simple, reliable tests (e.g., commonly used industrial methods) were found, they have been presented as well.

11.1 Quantitative Method for the Detection of Vinyl Chloride in Air

11.1.1 Gas Chromatography (NIOSH 1977; CIAL 1977). A range of 0.008 to 5.2 mg/m^3 (3.2 ppb to 2.01 ppm) of vinyl chloride in air may be determined by gas chromatography using flame ionization detection.

A known volume of air is drawn through two 7 cm x 6 mm O.D. charcoal tubes containing 2 sections of 20/40 mesh activated charcoal separated by a 2 mm portion of urethane foam. The first section contains 100 mg whereas the second, or back-up, section contains 50 mg. A silanized glass wool plug is placed before the front absorbing section. A sample size of 5 L is recommended. It is collected at a flow rate of 50 mL/min.

Both charcoal tube samples are scored before the first section of charcoal and broken. The larger section of charcoal is transferred to a 2 mL stoppered sample container containing 1.0 mL of carbon disulphide. The same operation is performed with the back-up section. The samples should be allowed to desorb for 30 minutes. A 5 µL aliquot of sample is injected into a gas chromatograph equipped with a flame ionization detector.

The vinyl chloride is determined using retention times and an electronic integrator which determines peak area, as well as a calibration curve. Typical gas chromatograph operating conditions are: helium carrier gas at 40 mL/min, hydrogen gas at 65 mL/min, air flow at 500 mL/min, injector temperature at 230°C, detector temperature at 230°C, and a column temperature of 60°C. The column is 0.6 x 548.6 cm (0.25 x 216 in.) stainless steel packed with chromosorb W.

11.2 Qualitative Method for the Detection of Vinyl Chloride in Air

Vinyl chloride may be determined in air by the use of a Drager detector tube for vinyl chloride. A volume of air is drawn through a Drager detector tube for vinyl chloride using a multi-gas detector pump; a change in colour of the violet indicating layer to pale brown indicates vinyl chloride (Drager 1979).

11.3 Quantitative Method for the Detection of Vinyl Chloride in Water

11.3.1 Partition Infrared (AWWA 1981). A range of 40 to 400 ppm (40 to 400 µg/mL) of vinyl chloride in water may be determined by partition infrared spectrophotometry. A minimum of 1 L of representative sample is collected in an appropriate container.

The sample is acidified to pH 2 by the addition of approximately 5 mL of 50 percent hydrochloric acid. The sample is then transferred to a separatory funnel and the sample container rinsed with 30 mL of Freon® 113 (1,1,2-trichloro-1,2,2-trifluoroethane). The solvent rinse is added to the separatory funnel. The solvent layer is drained into a 100 mL volumetric flask. The aqueous layer is extracted with two more 30 mL portions of solvent. The solvent extracts are combined in the volumetric flask and the volume taken to mark with solvent.

The vinyl chloride is determined using 1 cm matched near infrared silica cells and a double-beam recording I.R. spectrophotometer. The sample is scanned from 3200 to 2700 cm^{-1} with solvent in the reference beam. A standard curve is used to determine the quantity of vinyl chloride in the sample.

11.4 Qualitative Method for the Detection of Vinyl Chloride in Water

Vinyl chloride may be determined qualitatively in water by infrared spectroscopy. A sample is collected and extracted with Freon® 113 (1,1,2-trichloro-1,2,2-trifluoroethane) as in Section 11.3.1. The sample is scanned from 3200 cm^{-1} to 2700 cm^{-1} using a double-beam recording infrared spectrophotometer with Freon® in the reference cell. The presence of a characteristic absorbance pattern on the chromatogram indicates the presence of vinyl chloride (AWWA 1981).

11.5 Quantitative Method for the Detection of Vinyl Chloride in Soil

11.5.1 Infrared Spectrophotometry (AWWA 1981). A range of 40 to 400 ppm (40 to 440 µg/mL) vinyl chloride in soil may be determined using infrared spectrophotometry.

Approximately 20 g of soil, accurately weighed, are collected in a glass jar and dried by the addition of magnesium sulphate. Freon® 113 (1,1,2-trichloro-1,2,2-trifluoroethane) is used to extract the vinyl chloride from the soil. Using 1 cm matched quartz cells with Freon® in the reference beam of a double-beam I.R. recording spectrophotometer, the sample is scanned from 3200 to 2700 cm^{-1}. The vinyl chloride is determined using a calibration curve.

11.6 Qualitative Method for the Detection of Vinyl Chloride in Soil

Vinyl chloride may be determined qualitatively in soil by infrared spectroscopy. A sample is collected and extracted with Freon® 113 (1,1,2-trichloro-1,2,2-trifluoroethane) as in Section 11.5.1. The sample is scanned from 3200 to 2700 cm^{-1} using a double-beam recording spectrophotometer with Freon® in the reference cell. The presence of a characteristic absorbance pattern on the chromatogram indicates the presence of vinyl chloride (AWWA 1981).

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EnviroTIPS

Common Abbreviations

BOD	biological oxygen demand
b.p.	boiling point
CC	closed cup
cm	centimetre
CMD	count median diameter
COD	chemical oxygen demand
conc	concentration
c.t.	critical temperature
eV	electron volt
g	gram
ha	hectare
Hg	mercury
IDLH	immediately dangerous to life and health
Imp. gal.	imperial gallon
in.	inch
J	joule
kg	kilogram
kJ	kilojoule
km	kilometre
kPa	kilopascal
kt	kilotonne
L	litre
lb.	pound
LC_{50}	lethal concentration fifty
LC_{LO}	lethal concentration low
LD_{50}	lethal dose fifty
LD_{LO}	lethal dose low
LEL	lower explosive limit
LFL	lower flammability limit
m	metre
m	meta
M	molar
MAC	maximum acceptable concentration
max	maximum
mg	milligram
MIC	maximum immission concentration
min	minute or minimum
mm	millimetre
µg	microgram
µm	micrometre
°Be	degrees Baumé (density)
MMAD	mass median aerodynamic diameter
MMD	mass median diameter
m.p.	melting point
MW	molecular weight
N	newton
NAS	National Academy of Sciences
NFPA	National Fire Protection Association
NIOSH	National Institute for Occupational Safety and Health
nm	nanometre
o	ortho
OC	open cup
p	para
P_c	critical pressure
PEL	permissible exposure level
pH	measure of acidity/alkalinity
ppb	parts per billion
ppm	parts per million
P_s	standard pressure
psi	pounds per square inch
s	second
STEL	short-term exposure limit
STIL	short-term inhalation limit
T_c	critical temperature
TC_{LO}	toxic concentration low
Td	decomposition temperature
TD_{LO}	toxic dose low
TL_m	median tolerance limit
TLV	Threshold Limit Value
Ts	standard temperature
TWA	time weighted average
UEL	upper explosive limit
UFL	upper flammability limit
VMD	volume mean diameter
v/v	volume per volume
w/w	weight per weight